Synthesis of Aminophosphine Derivatives by Chloramination and Chlorophosphination Reactions

By
HARBHAJAN SINGH AHUJA

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
February, 1962

ACKNOWLEDGMENTS

The author takes this opportunity to express his sincere appreciation and deep gratitude to his research director and teacher, Dr. Harry H. Sisler, for his aid and guidance in carrying out this research work and in the writing of this dissertation. Dr. Sisler has been a constant source of encouragement throughout the course of this work. His encouraging words on numerous occasions helped in lifting the sinking morale of the author.

Appreciation is extended to other members of the author's Graduate Supervisory Committee for making suggestions in the writing of this dissertation.

The author wishes to express his sincere gratitude to Dr. W. S. Brey, Jr., of the Chemistry Department of the University of Florida under whose direction the nuclear magnetic resonance spectra were determined and interpreted.

Special thanks should go to Mr. N. L. Smith for giving so generously of his time and the benefit of his many years of experience during the earlier phases of this research.

The author is grateful to his laboratory partners, fellow graduate students, faculty, and the staff of the Chemistry Department for the help furnished by them, directly or indirectly, during the course of this work.

Thanks also is due to Mrs. Penny Ansell who, with a great deal of patience and against so many odds, typed this dissertation. Thanks to Miss Gini Lenz for drawing the figures.

The author wishes to express his gratitude to W. R. Grace and Company whose generous financial support made this research work possible.

TABLE OF CONTENTS

		Page
ACKNOWLEDGMENTS		ii
LIST OF TABLES		v
LIST OF FIGURES		vi
Chapters		
I	REACTIONS OF TRISUBSTITUTED PHOSPHINES WITH CHLORAMINE: THE PREPARATION OF TRISUBSTITUTED AMINOPHOSPHONIUM SALTS	1
	Introduction	1
	Purpose of Investigation	1
	Historical Background	2
	Materials	6
	Experimental and Results	6
	Discussion	32
II	STUDIES IN THE SYNTHESIS OF SUBSTITUTED PHOSPHONITRILIC POLYMERS	39
	Introduction	39
	Purpose of Investigation	39
	Historical Background	42
	Materials	50
	Experimental and Results	50
	Discussion	74
III	SYNTHESIS OF N-SUBSTITUTED AMINODIBUTYLPHOSPHINES	84
	Introduction	84
	Purpose of Investigation	84

TABLE OF CONTENTS
Continued

	Page
Historical Background	84
Materials	86
Experimental and Results	87
Discussion	98
BIBLIOGRAPHY	102
APPENDIX	107
BIOGRAPHICAL SKETCH	108

LIST OF TABLES

Table		Page
1.	P-Tri-n-butylaminophosphonium Salts	9
2.	P-Phenyl-P,P-(cyclotetramethylene)-aminophosphonium Salts	12
3.	P-Phenyl-P,P-(cyclopentamethylene)-aminophosphonium Salts	16
4.	P-Tribenzylaminophosphonium Salts	20
5.	P-Tris-(2-cyanoethyl)-aminophosphonium Salts	23
6.	P-Phenyl-P,P-(diallyl)-aminophosphonium Salts	26
7.	A Summary of Reactions of Diphenylchlorophosphine-Ammonia and Chloramine	65
8.	Analyses of Compound II and Its Derivatives	72

LIST OF FIGURES

Figure		Page
1.	Chloramine Generator	7
2.	Infrared Spectrum of Oxide from Hydrolyzed P-tri-n-butylaminophosphonium Chloride	31
3.	Infrared Spectrum of Tri-n-butylphosphine Oxide	31
4.	Infrared Spectrum of P-tribenzylaminophosphonium Chloride	33
5.	Infrared Spectrum of P-tri-n-butylaminophosphonium Chloride	33
6.	High Vacuum Closed System	55
7.	Infrared Spectrum of Compound I	68
8.	Infrared Spectrum of Diphenylphosphonitrilic Trimer	68
9.	Infrared Spectra of the Intermediate Obtained by Bezmann and Smalley from Diphenylphosphorus Trichloride-Ammonia	70
10.	Infrared Spectrum of Compound II	70
11.	Infrared Spectrum of Compound II (15 to 38 Micron Region)	73
12.	Infrared Spectrum of the Hexafluorophosphate Derivatives of Compound II (15 to 38 Micron Region)	73

CHAPTER 1

REACTIONS OF TRISUBSTITUTED PHOSPHINES WITH CHLORAMINE: THE PREPARATION OF TRISUBSTITUTED AMINOPHOSPHONIUM SALTS

Introduction

Purpose of Investigation

The N-aminating properties of chloramine were demonstrated by Raschig[1] in 1907 by the preparation of hydrazine, through the reaction of hypochlorite with an aqueous solution of ammonia,

$$NH_3 + OCl^- \longrightarrow NH_2Cl + OH^-$$

$$NH_3 + OH^- + NH_2Cl \longrightarrow N_2H_4 + Cl^- + H_2O$$

Aqueous chloramine was produced by the first step above. Raschig[2] also prepared phenylhydrazine in trace amounts by the reaction of chloramine and aniline in aqueous solutions. Later, various substituted hydrazines were prepared in aqueous solution by Audrieth and Diamond.[3,4] The synthesis of gaseous chloramine, by the gas phase reaction of chlorine and ammonia, by Sisler and Mattair[5] was the beginning of a new phase in the chemistry of chloramination. The simplicity of the preparation and the completely anhydrous nature of the product were the chief advantages of the Sisler-Mattair method. Sisler and his coworkers[6,7] reacted gaseous chloramine with liquid ammonia, and with primary, secondary, and tertiary amines to form hydrazine,

substituted hydrazines, and the 1,1,1-trisubstituted hydrazinium salts as shown by the following equations:

$$2NH_3 + NH_2Cl \longrightarrow NH_2NH_2 + NH_4Cl$$

$$2RNH_2 + NH_2Cl \longrightarrow R\text{-}NH\text{-}NH_2 + RNH_3Cl$$

$$2R_2NH + NH_2Cl \longrightarrow R_2N\text{-}NH_2 + R_2NH_2Cl$$

$$R_3N + NH_2Cl \longrightarrow R_3N\text{-}NH_2\ ^{+}Cl^{-}$$

The reactions of chloramine were then extended to the next element of the nitrogen family of the periodic system, namely phosphorus. Sarkis[8] showed that triphenylphosphine reacts with chloramine under anhydrous conditions to form triphenylaminophosphonium chloride.

The present investigation was started to study the versatility of the reaction:

$$R_3P + NH_2Cl \longrightarrow [R_3PNH_2]^{+}Cl^{-}$$

when the substituents R attached to the phosphorus atom are altered, and more generally to explore the possibility of extending the gas phase chloramination reaction to a variety of tertiary phosphorus compounds in order to use the chloramination reaction as a synthetic tool for the preparation of organo-phosphorus compounds having P-N bonds.[9]

Historical Background

In 1919, Staudinger[10,11] prepared substituted phosphinimines by the reaction of tertiary phosphines with azides.

$$R_3P + RN_3 \longrightarrow R_3\overset{+}{P}\text{-}N\text{=}N\text{-}\overset{-}{N}\text{-}R \longrightarrow R_3P\text{=}NR + N_2$$

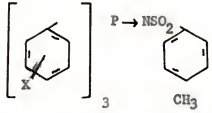
He could not isolate the pure phosphinimines but was successful in preparing the hydrazoic salts of triethyl and triphenyl phosphinimines.

$$R_3P + 2HN_3 \longrightarrow [R_3P{=}NH]HN_3 + N_2$$

The nature of bonding in these compounds is not known but most probably these were the first compounds having the aminophosphonium ion:

$$[R_3PNH_2]^+N_3^-$$

In 1937, Mann and Chaplin[12] studied the polarity of the P-N bond formed in the reaction of chloramine-T with triaryl phosphines by changing the ortho and para substitution in the phenyl ring of the aryl phosphine.



Other synthetic routes for the preparation of the substituted phosphinimines and related compounds are also known.[13,14,15]

Sarkis[8] studied the reaction of chloramine and N-methyl chloramine, prepared by the Raschig method, with triphenylphosphine. He prepared triphenylaminophosphonium and triphenyl-N-methylaminophosphonium chlorides. The identity of the aminophosphonium ion was established by the formation of various stable derivatives.

Recently a great variety of substituted phosphinimines and aminophosphonium salts were prepared by Horner and Oediger[16] by the reaction of triphenylphosphorus dihalides with amines.

$$ArNH_2 + (C_6H_5)_3PX_2 \xrightarrow[-2HX]{2N(C_2H_5)_3} Ar\text{-}N{=}P(C_6H_5)_3$$

I

$$\xrightarrow[-HX]{\text{pyridine}} \left[Ar\text{-}\overset{H}{\underset{|}{N}}\text{-}P(C_6H_5)_3\right]^+ X^-$$

II

The course of the reaction depends upon the basicity of the amine used and also on the tertiary aliphatic amine employed to remove the hydrogen halide formed in the reaction. In the above case of aniline, if the reaction is carried out in the presence of triethyl amine, a phosphinimine is formed (I), but when pyridine is used the reaction stops at the first step after the removal of one molecule of hydrogen halide and the resulting compound is a N-substituted aminophosphonium salt (II). By using the primary aliphatic amine and the triphenyl phosphorus dihalide, only the N-substituted aminophosphonium salts are formed which could not be further converted to the phosphinimines.

During the course of preparation of substituted aminophosphonium salts, Horner and Oediger[16] prepared triphenylaminophosphonium bromide by the reaction of triphenylphosphorus dibromide and ammonia.

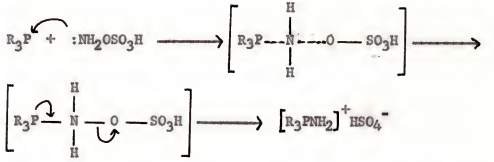
$$(C_6H_5)_3PBr_2 + NH_3 \xrightarrow{\text{pyridine}} \left[(C_6H_5)_3PNH_2\right]^+ Br^- + HBr$$

Appel, Buchner and Guth[17] made an attempt to prepare triphenylphosphinimine by the following reaction:

$$(C_6H_5)_3P + H_2NOSO_3H + 2NaOCH_3 \xrightarrow{MeOH} (C_6H_5)_3P{=}NH + Na_2SO_4 + CH_3OH$$

but the phosphinimine is easily decomposed and when they worked up the products of the above reaction, triphenylphosphine oxide and some unreacted triphenylphosphine was isolated. However, in order to stabilize the phosphinimine through salt formation, the above reaction was repeated, this time taking less than the stoichiometric amount of sodium methoxide required for the reaction. From the reaction products they isolated a water soluble salt, triphenylaminophosphonium hydrogen-sulfate $[(C_6H_5)_3PNH_2]^+HSO_4^-$. The identity of the aminophosphonium ion was established by the formation of picrate and other insoluble derivatives.

The probable mechanism for the formation of the aminophosphonium salts is explained by the nucleophilic attack of the hydroxyamine-O-sulfonic acid on the phosphorus atom of the tertiary phosphine, such as:



Appel and Hauss[18] prepared aromatic, aliphatic, as well as mixed aromatic and aliphatic aminophosphonium chlorides and their salts by the reaction of the gaseous chloramine and the corresponding phosphines. The procedure was essentially the same as used in this investigation and had been published prior to the Appel and Hauss publication.[19]

Materials

Tri-n-butylphosphine is commercially available. P-phenyl-P,P-(cyclotetramethylene)-phosphine and P-phenyl-P,P-(cyclopentamethylene)-phosphine were prepared by the method of Gruttner.[20] P-tribenzylphosphine was prepared by the method of Hinton and Mann.[21] P-tri-(a-cyanoethyl)-phosphine was kindly supplied by Dr. Rauhut of American Cyanamid Company. P-phenyl-P,P-(diallyl)-phosphine was prepared by the procedure of Jones et al.[22] Tris-(m-trifluoromethylphenyl)-phosphine was prepared for the first time by the reaction of phosphorus trichloride with the appropriate Grignard reagent. Gaseous chloramine was prepared by the gas phase reaction of ammonia and chlorine. The design of the chloramine generator was essentially as described by Sisler and Omietanski.[9] The mole ratio of ammonia to chloramine was approximately 30:1. The amount of chloramine produced was about 0.1 mole per hour.

Unless otherwise stated, all microanalyses were done by Galbraith Laboratories, Knoxville, Tennessee. The melting points are uncorrected.

Experimental and Results

The Chloramination of Tri-n-butylphosphine

A typical reaction of tri-n-butylphosphine with chloramine is described. To a solution of 9.0 grams (0.0445 mole) of phosphine in 60 ml. of sodium dried ether, chloramine gas from the generator was bubbled for 20 minutes. The reaction vessel was chilled with an ice bath during the reaction. At the end of the reaction the products were

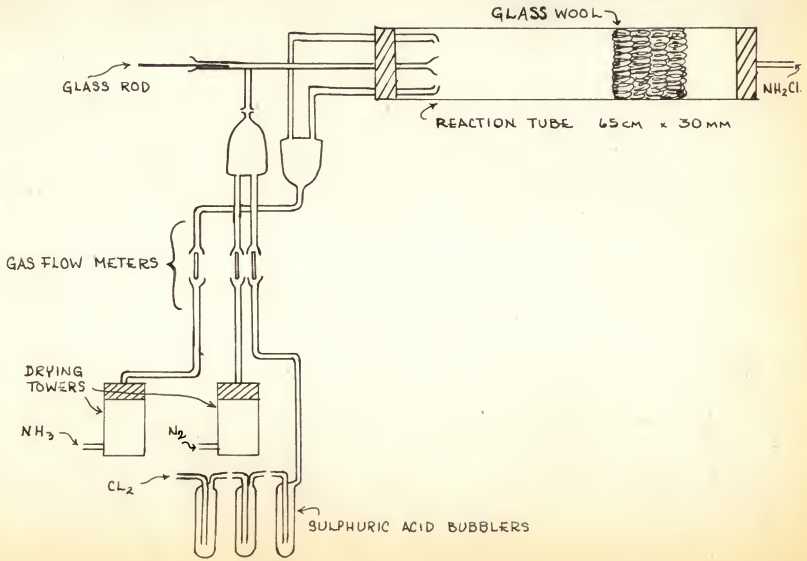


Fig. 1 Chloramine Generator

filtered, washed with ether and the solid dried in a vacuum desiccator. It weighed 6.8 grams and melted between 62-65°C. in a sealed tube. From the filtrate and washings 3.3 grams of unreacted phosphine was recovered. The chloride analysis of the solid was 14.02 per cent (Volhard's method). Calculated for $[(C_4H_9)_3PNH_2]^+Cl^-$: 13.97 per cent yield. The yield is quantitative based on the amount of phosphine used. Analytical results are shown in Table 1.

Tri-n-butylaminophosphonium chloride is a colorless, shining, white solid. It is very hygroscopic and if kept in the open for a few minutes, it turns to an oily liquid. It can be stored in a desiccator for a long time without any change. It is readily soluble in water and ethanol. In these solutions it forms a large number of derivatives such as the hexafluorophosphate, the perchlorate, the hexachloroplatinate, the picrate, and the anthraquinone-β-sulfonate.

P-Tri-n-butylaminophosphonium Hexafluorophosphate. P-Tri-n-butylaminophosphonium hexafluorophosphate was prepared by simple metathesis, by mixing the aqueous solution of the tributylaminophosphonium chloride and aqueous solution of the potassium salt of the nexafluorophosphate. The precipitate was filtered and dried at 45°C. It melted at 72-73°C. The analytical results shown in Table 1 agree with the formula:

$$[(C_4H_9)_3PNH_2]^+PF_6^-$$

P-Tri-n-butylaminophosphonium Anthraquinone-β-sulfonate. P-Tri-n-butylaminophosphonium anthraquinone-β-sulfonate was prepared in the aqueous solution by mixing the sodium salt of anthraquinone- -sulfonate

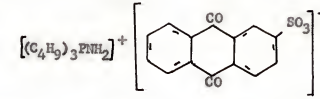
TABLE 1

P-(Tri-n-butyl)-aminophosphonium Salts $\left[(C_4H_9)_3PNH_2\right]^+X^-$

Salt X^-	Melting Point °C.	Empirical Formula	Analyses %C Calcd. Found	%H Calcd. Found	%N Calcd. Found	%P Calcd. Found	% Calcd. Found
Chloride	62-65 (sealed tube)	$C_{12}H_{29}ClNP$	56.78	11.52 11.65	5.52 5.48	12.21	13.97[a] 14.02
Hexafluorophosphate	72-73	$C_{12}H_{29}F_6P$	39.67 39.67	8.04 7.92	3.86 3.92	17.05 16.91	---
Anthraquinone-β-sulfonate	89-90	$C_{26}H_{36}NO_7SP$	61.76 61.32	7.18 7.07	2.77 2.77	6.13 6.11	6.39[b]
Perchlorate	86-89	$C_{12}H_{29}ClNPO_4$	45.35 44.98	9.18 9.00	4.41 4.98	9.75 10.98	---

[a]Chloride. [b]Sulfur.

and the aminophosphonium chloride. After drying, it melted at 89-90°C. The analytical results shown in Table 1 agree with the formula:



P-Tri-n-butylaminophosphonium Perchlorate. P-Tri-n-butylaminophosphonium perchlorate was prepared in similar manner as described earlier, in aqueous solutions. After drying, it melted at 86-89°C. The analytical results shown in Table 1 agree with the formula:

$$[(C_4H_9)_3PNH_2]^+ClO_4^-$$

P-Tri-n-butylaminophosphonium Picrate. P-Tri-n-butylaminophosphonium picrate was prepared in the ethanolic solutions using picric acid. After drying, it melted at 72-74°C.

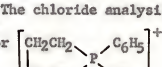
P-Tri-n-butylaminophosphonium Hexachloroplatinate. P-Tri-n-butylaminophosphonium hexachloroplatinate was prepared in similar manner using a 10 per cent solution of hexachloroplatinic acid. After drying, it melted at 140-142°C.

The Chloramination of P-Phenyl-P,P-(cyclotetramethylene)-phosphine

Preparation of P-Phenyl-P,P-(cyclotetramethylene)-phosphine. To a solution of the Grignard reagent, prepared from 100.0 grams (0.46 mole) of 1,4-dibromobutane in one liter of ether and 34.0 grams (1.4 moles) of magnesium in 250 ml. of ether, there was added 50.0 grams (0.27 mole) of phenyldichlorophosphine under nitrogen. The resulting solution was maintained under reflux for one hour. The crude product

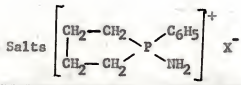
was isolated by distillation under nitrogen atmosphere. Redistillation provided a colorless liquid, boiling at 98-100°C. at 2 mm. of pressure (reported 132-133°C. at 16-18 mm.), which weighed 15.0 grams (19 per cent yield).

Reaction with Chloramine. Two reactions were carried out in anhydrous ether as solvent, and in neither case could pure aminophosphonium chloride be obtained. The solid isolated from the reaction in each case contained a small amount of ammonium chloride as an impurity. However, a number of crystalline, stable derivatives were prepared and characterized. These establish the formation of aminophosphonium chloride from the above reaction. Typical reactions are described below:

1) A gaseous mixture of the chloramine and ammonia was passed through a solution of the phosphine (2.0 grams) in 40 ml. of anhydrous ether for 10 minutes. The reaction flask was surrounded with an ice bath during the passage of the gases. The product was filtered, washed with ether and vacuum dried. The chloride analysis of the solid was 19.83 per cent. Calculated for  Cl^-: 16.44 per cent. This showed an impurity of about 5.7 per cent of ammonium chloride in the product. A major portion of this product in the melting point tube melted at 110-112°C. A water solution of this impure product reacted with anions such as picrate, hexafluorophosphate, etc., to form the insoluble derivatives.

2) In a second experiment the above procedure was essentially repeated using 5.0 grams of the phosphine in 45 ml. of the ether, and

TABLE 2

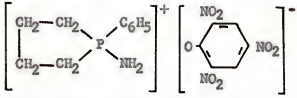
P-Phenyl-P,P-(cyclotetramethylene)-aminophosphonium Salts 

Salt X^-	Melting Point °C.	Empirical Formula	Analyses %C Calcd. Found	%H Calcd. Found	%N Calcd. Found	%P Calcd. Found	% Calcd. Found
Chloride[a]	110-112	$C_{10}H_{15}ClNP$	-	-	-	-	16.44[b] 19.83
Hexafluorophosphate	76-77	$C_{10}H_{15}F_6NP_2$	36.93 36.14	4.65 4.82	4.31 4.39	-	
Anthraquinone-β-sulfonate	207-208	$C_{24}H_{22}NO_7SP$	61.66 60.88	4.74 4.78	3.00 3.11	6.83 6.66	
Picrate	171-172	$C_{66}H_{17}N_4O_7P$	47.06 48.82	4.02 3.99	13.72 13.91	7.59 7.50	

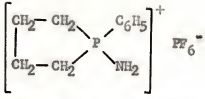
[a]Impure. [b]Chloride.

chloramine was passed for 17 minutes. The products were filtered, washed with ether and vacuum dried. The chloride analysis of the reaction product was 18.10 per cent. Calculated: 16.44 per cent. This corresponds to about 3.3 per cent of ammonium chloride impurity. The major portion of the solid in the melting point tube this time melted at 108-110°C. The impure salt was used to prepare various derivatives.

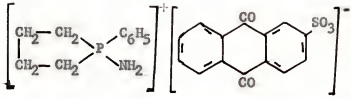
P-Phenyl-P,P-(cyclotetramethylene)-aminophosphonium Picrate. P-phenyl-P,P-(cyclotetramethylene)-aminophosphonium picrate was prepared by treating the aqueous solution of the product with picric acid in water. The solid was immediately filtered and vacuum dried. It melted at 177-178°C. On recrystallization in ethanol, shining yellow crystals were obtained which melted at 171-172°C. The analytical data given in Table 2 agree with the formula:



P-Phenyl-P,P-(cyclotetramethylene)-aminophosphonium Hexafluorophosphate. P-phenyl-P,P-(cyclotetramethylene)-aminophosphonium hexafluorophosphate was prepared by mixing the water solution of the impure aminophosphonium chloride and a saturated solution of potassium hexafluorophosphate. The resulting solution was kept on ice. Upon standing for some time, a white crystalline solid separated out from the solution. It melted at 76-77°C. The analytical data given in Table 2 agree with the formula:



P-Phenyl-P,P-(cyclotetramethylene)-aminophosphonium Anthraquinone-β-sulfonate. P-phenyl-P,P-(cyclotetramethylene)-aminophosphonium anthraquinone-β-sulfonate was prepared by simple metathesis of a water solution of the sodium salt of the anthraquinone-β-sulfonate with the water solution of the product. A bulky white precipitate immediately separated. This was recrystallized from methanol. The melting point was 207-208°C. The analytical data shown in Table 2 agree with the formula:

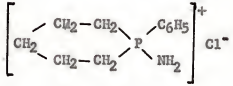


The Chloramination of P-Phenyl-P,P-(cyclopentamethylene)-phosphine

Preparation of P-Phenyl-P,P-(cyclopentamethylene)-phosphine. A solution of 15.0 grams (0.08 mole) of phenyldichlorophosphine in 100 ml. of ether was added with constant stirring to a Grignard reagent prepared from 23.0 grams (0.1 mole) of 1,5-dibromopentane and 7.2 grams (0.3 mole) of magnesium metal in 150 ml. of ether. Gentle reflux was maintained throughout the addition. After stirring under reflux for an additional hour, the mixture was distilled under reduced pressure to remove the solvent. The crude product was obtained after distillation from a metal bath under nitrogen. Redistillation provided a slightly yellowish liquid

boiling at 106°C./3mm. (reported 153-154°C./22-24mm.). The liquid weighed 2.0 grams (yield 13 per cent).

Reaction with Chloramine. Chloramine and ammonia mixture from the generator was bubbled through a solution of 2.0 grams of the phosphine in 40 ml. of anhydrous ether for a period of 10 minutes. The reaction tube was maintained at an ice cold temperature during the reaction. At the end of the run the reaction products were filtered, washed with ether, and the solid was vacuum dried. The chloride analysis of the solid was 14.77 per cent (Volhard method). The calculated value from the formula,



is 15.45 per cent. The solid melted near 76°C. but could not be further purified by recrystallization from the usual solvents.

The aminophosphonium ion in this mixture was characterized by the formation of stable derivatives.

P-Phenyl-P,P-(cyclopentamethylene)-aminophosphonium Picrate. P-phenyl-P,P-(cyclopentamethylene)-aminophosphonium picrate was prepared in the aqueous solution and recrystallized with methanol. It melted at 151-152°C. The analytical data given in Table 3 agree with the formula:

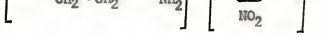
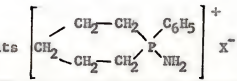


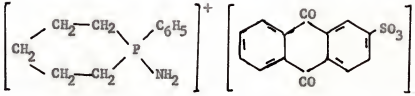
TABLE 3

P-Phenyl-P,P-(cyclopentamethylene)-aminophosphonium Salts 

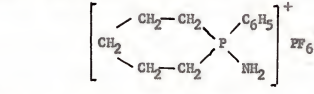
Salt X^-	Melting Point °C.	Empirical Formula	Analyses %C Calcd. Found	%H Calcd. Found	%N Calcd. Found	%P Calcd. Found	% Calcd. Found
Chloride[a]	76-77	$C_{11}H_{15}ClNP$	-	-	-	-	15.45 14.77[b]
Hexafluorophosphate	120-121	$C_{11}H_{17}F_6NP_2$	38.95 38.86	5.05 5.08	4.13 4.39	18.26 17.98	-
Anthraquinone-β-sulfonate	243 (decomp)	$C_{25}H_{24}NO_7SP$	62.36 61.42	5.02 5.17	2.91 3.32	6.43 6.43	
Picrate	150-151	$C_{22}H_{21}N_4O_7P$	-	-	13.33 13.11	7.37 7.25	

[a]Impure. [b]Chloride.

P-Phenyl-P,P-(cyclopentamethylene)-aminophosphonium Anthraquinone-β-sulfonate. P-phenyl-P,P-(cyclopentamethylene)-aminophosphonium anthraquinone-β-sulfonate was prepared in aqueous solution. The crude product melted at 242°C. After the recrystallization from absolute ethanol, the melting point was 243°C. The color of this compound was light pink. The analytical data given in Table 3 agree with the formula:



P-Phenyl-P,P-(cyclopentamethylene)-aminophosphonium Hexafluorophosphate. P-phenyl-P,P-(cyclopentamethylene)-aminophosphonium hexafluorophosphate was prepared in aqueous solution and recrystallized from methanol. The melting point was 120-121°C. The analytical date given in Table 3 agree with the formula:



The Chloramination of P-Tribenzylphosphine

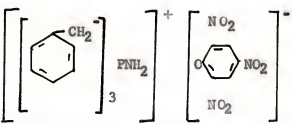
Preparation of the P-Tribenzylphosphine. The phosphine was prepared by the reaction of benzylmagnesium chloride and phosphorus trichloride in ether solution. The resultant product after the removal of the solvent was distilled at reduced pressure. The solid phosphine obtained melted at 92-95°C. (literature value 92-95°C.).

Reaction with Chloramine. Chloramination of tribenzylphosphine was carried out in three different solvents. In anhydrous ether, the phosphine has a low solubility. However, chloramination does take place in ether, but the resultant product is generally contaminated with the starting material. The phosphine is completely soluble in methylene chloride, but the solubility of the corresponding aminophosphonium chloride in the methylene chloride somewhat complicates the separation. Best results were obtained by using sodium-dried benzene as the solvent. Two experiments are described here:

1) Into a solution of 1.3 grams of the phosphine (4.28 mmoles) in 60 ml. of methylene chloride, chloramine from the generator was passed for 20 minutes at ice-bath temperature. A white turbidity slowly developed, and at the end of the run a white precipitate separated out. The products were filtered and washed with an additional 40 ml. of the solvent. The insoluble portion was vacuum dried (weight 1.3 grams). The chloride analysis of this solid was 64.65 per cent. Calculated for ammonium chloride: 66.29 per cent. Therefore the solid is essentially ammonium chloride. The solvent was removed from the filtrate under reduced pressure. The residue so obtained weighed 1.29 grams. This was yellowish in appearance and somewhat tacky in nature. It softened over a long range of temperature. Only a small portion of this solid dissolved in cold water. After drying this solid at 80°C./3 mm. for two hours, the chloride content was determined. The total soluble chloride of this product was 12.90 per cent. Calculated for $[(C_6H_5CH_2)_3PNH_2]^+Cl^-$: 9.97 per cent. The water solution reacted with the various anions giving various aminophosphonium derivatives, thus indicating that chloramination had taken place.

2) Into a solution of 0.955 grams (3.14 mmoles) of phosphine in 80 ml. of sodium-dried benzene at 25°C., was passed 8.3 mmoles of chloramine in the form of chloramine-ammonia mixture from the chloramine generator. The resultant crystalline product was washed with dry benzene and dried under vacuum (weight 0.745 grams, 2.09 mmoles, calculated as $(C_6H_5CH_2)_3PNH_2Cl$). This, after recrystallization from hot chloroform melted at 220-221°C. The analytical results are in agreement with the formula, $[(C_6H_5CH_2)_3PNH_2]^+Cl^-$, and are listed in Table 4. Evaporation of the liquid phase yielded 0.325 grams (1.06 mmoles) of unreacted tribenzylphosphine contaminated with the corresponding oxide impurity. The yield of the aminophosphonium salt is virtually quantitative based on the amount of phosphine used. The tribenzylaminophosphonium ion was further confirmed by the preparation of the picrate and hexachloroplatinate derivatives.

P-Tribenzylaminophosphonium Picrate. P-tribenzylaminophosphonium picrate was prepared by metathesis with picric acid in aqueous solution. On recrystallization from ethanol, it melted at 179.5-180.5°C. The analytical data shown in Table 4 agree with the formula:



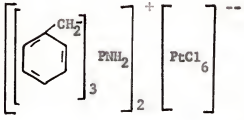
P-Tribenzylaminophosphonium Hexachloroplatinate. P-tribenzylaminophosphonium hexachloroplatinate was prepared by mixing a 10 per cent aqueous solution of hexachloroplatinic acid with the aminophosphonium chloride in water. The solid was filtered, and after drying, melted

TABLE 4

P-Tribenzylaminophosphonium Salts $[(C_6H_5CH_2)_3PNH_2]^+X^-$

Salt X^-	Melting Point °C.	Empirical Formula	Analyses %C Calcd. Found	%H Calcd. Found	%N Calcd. Found	%P Calcd. Found	%Cl Calcd. Found
Chloride	220-221	$C_{21}H_{23}ClNP$	70.88 70.76	6.51 7.01	3.94 3.84	8.71 8.90	9.97 10.10
Picrate	179.5-180.5	$C_{27}H_{25}N_4O_7P$	59.12 58.74	4.59 4.91	10.22 10.00	5.65 5.77	--- ---
Hexachloroplatinate	190-191	$C_{42}H_{46}Cl_6N_2P_2Pt$	48.10 45.64	4.42 4.43	2.67 2.49	5.91 5.71	20.29 22.96

at 190-191°C. The analytical data given in Table 4 agree with the formula:



The Chloramination of Tris-(2-cyanoethyl)-phosphine

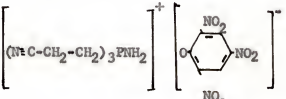
Tris-(2-cyanoethyl)-phosphine was kindly supplied by Dr. Rauhut of the American Cyanamid Company and melted at 96-98°C. (reported 96-98°C.).

Reaction with Chloramine. The chloramination of the phosphine was carried out in ether and methylene chloride. The phosphine is slightly soluble in ether at room temperature but readily dissolves in methylene chloride. Two reactions in these solvents are described below:

1) The gaseous effluent from the chloramine generator was passed into a solution of 0.7 gram (3.6 mmoles) of the phosphine in 70 ml. of dry ether for ten minutes. The precipitate appeared after some time. The reaction products were filtered and washed twice with 50 ml. portion of ether. The solid after drying weighed 1.0 grams. This solid partly dissolved in water, and the water solution reacted with picric acid and potassium hexachloroplatinate to form the usual derivatives. The water insoluble solid melted at 94-96°C. and was the starting material. This indicates that only a part of the phosphine has reacted with the chloramine. From the filtrate and the washings, 0.2 grams of tacky solid was obtained after the complete removal of ether.

2) The gaseous effluent of the chloramine generator (approximately 5 mmoles) was bubbled through a solution of 0.533 grams of tris-(2-cyanoethyl)-phosphine (2.76 mmoles) in 80 ml. of dry methylene chloride. The resultant crystalline solid was washed with dry methylene chloride and vacuum dried at room temperature. Chloride analysis gave 16.21 per cent chlorine (Volhard method). Calculated for $[(N{\equiv}CCH_2CH_2)_3PNH_2]^+Cl^-$: 14.49 per cent chlorine. This indicates about 3.3 per cent ammonium chloride contamination with the aminophosphonium chloride. The yield of the crude product is approximately 85 per cent based on the amount of phosphine reacted. This solid could not be freed from the ammonium chloride by recrystallization from polar solvents. The identity of the aminophosphonium ion was established by the formation of picrate and hexachloroplatinate derivatives in aqueous solutions where ammonium chloride does not interfere.

Tris-(2-cyanoethyl)-aminophosphonium Picrate. Tris-(2-cyanoethyl)-aminophosphonium picrate was prepared in the aqueous solution and recrystallized from ethanol. The melting point was 154°C. The analytical data given in Table 5 agree with the formula:



Tris-(2-cyanoethyl)-aminophosphonium Hexachloroplatinate. Tris-(2-cyanoethyl)-aminophosphonium hexachloroplatinate was prepared by simple metathesis in aqueous solution between hexachloroplatinic acid

TABLE 5

P-Tris-(2-cyanoethyl)-aminophosphonium Salts $\left[(N{\equiv}C\text{-}CH_2\text{-}CH_2)_3PNH_2\right]^+X^-$

Salt X^-	Melting Point °C.	Empirical Formula	Analyses %C Calcd. Found	%H Calcd. Found	%N Calcd. Found	%P Calcd. Found	%Cl Calcd. Found
Chloride[a]	---	$C_9H_{14}NP$	---	---	---	---	14.49[b] 16.21
Picrate	154	$C_{15}H_{16}N_7O_7P$	41.19 40.03	3.68 3.75	7.08 6.85	22.42 22.35	---
Hexachloroplatinate	201 (decomp)	$C_{18}H_{28}Cl_6N_8P_2Pt$	26.16 26.55	3.41 3.88	7.50 7.71	13.56 12.98	25.75 25.33

[a]Impure. [b]Chloride.

and the impure chloride. It melted at 201°C. with decomposition. The analytical data given in Table 5 agree with the formula:

$$\left[(N{\equiv}C\text{-}CH_2\text{-}CH_2)_3PNH_2\right]_2^{+}\left[PtCl_6\right]^{=}$$

The Chloramination of P-Phenyl-P,P-(diallyl)-phosphine

Preparation of the P-Phenyl-P,P-(diallyl)-phosphine. To a solution of 7.2 grams (0.5 mole) of allylmagnesium bromide in 300 ml. of ether, 17 ml. of phenyldichlorophosphine (0.125 mole) in 100 ml. of ether was added slowly during two hours. The temperature of the reaction flask was maintained between 0-10°C. during the addition. The resultant product was treated with 50 grams of NH_4Cl in 250 ml. of water. The ether layer was dried over Na_2SO_4 and after removal of ether the liquid was distilled. Seven and fifty-four hundredths grams of the phosphine distilled at 70-75°C./0.4 mm. (literature value 127°C./24 mm.).

Reaction with Chloramine. The chloramination of the phosphine was carried out in ether and in methylene chloride. The reaction in the methylene chloride solvent was complicated by the partial solubility of the reaction product in the solvent. The reaction in the ether solvent takes place in a straightforward way such that the aminophosphonium chloride formed precipitates from the ether and adheres to the walls of the reaction tube. Several reactions in the ether solvent were run but the chloride analysis of the solid obtained, differed slightly from the calculated value. This could be attributed to either the hydroscopic and adherent nature of the solid, which makes the analysis rather difficult to perform, or the presence of small amounts of ammonium chloride impurity. A typical reaction is described below:

To a solution of 2.91 grams (15.1 mmoles) of diallylphenylphosphine in 80 ml. of dry diethyl ether, approximately 25 mmoles of chloramine in the form of the gaseous ammonia-chloramine mixture was bubbled in at 25°C. A light yellow, tacky solid was formed on the sides of the reaction tube. The mixture was chilled to about -65°C. in the dry ice-acetone mixture and the mother liquor was decanted. The solid residue was washed with 30 ml. portions of diethyl ether by decantation. The reaction tube was kept cold while the solid was chipped from the sides of the tube. It weighed 2.94 grams (12.16mmoles calculated as

$$\left[(CH_2{=}CH{-}CH_2{-})_2\overset{C_6H_5}{\overset{|}{P}}NH_2\right]^{+} \; -\; Cl).$$

About 0.3 grams (1.50 mmoles) of unreacted phosphine was recovered from the filtrate. The solid product contained 15.72 per cent chlorine. Calculated for $\left[(CH_2{=}CH{-}CH_2)_2\overset{C_6H_5}{\overset{|}{P}}NH_2\right]^{+} Cl^{-}$: 14.72 per cent chlorine. The product is slightly impure, probably containing small amounts of ammonium chloride. The yield of the impure diallylphenylaminophosphonium chloride is about 90 per cent based on the phosphine reacted.

The identity of the aminophosphonium ion was established by preparation of the hexachloroplatinate and the anthraquinone-β-sulfonate derivatives. The data on these compounds are compiled in Table 6.

P-Phenyl-P,P-(diallyl)-aminophosphonium Anthraquinone-β-sulfonate. To the ethanolic solution of the aminophosphonium chloride, sodium salt of the anthraquinone-β-sulfonate was added. The precipitate obtained was quickly filtered and vacuum dried. The melting point was

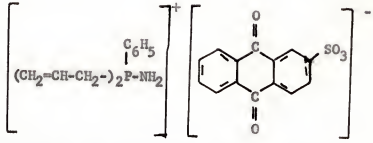
TABLE 6

P-Phenyl-P,P-(diallyl)-aminophosphonium Salts $\left[(CH_2{=}CH{-}CH_2)_2(C_6H_5)PNH_2\right]^+ X^-$

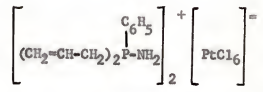
Salt X^-	Melting Point °C.	Empirical Formula	Analyses %C Calcd. Found	%H Calcd. Found	%N Calcd. Found	%P Calcd. Found	% Calcd. Found
Chloride[a]	---	$C_{12}H_{17}NP$	---	---	---	---	14.67[b] 15.72
Anthraquinone-β-sulfonate	181-183	$C_{26}H_{24}NO_5PS$	63.27 63.68	4.90 5.02	2.84 2.91	6.28 6.41	6.50[c] 6.85
Hexachloroplatinate	192-193	$C_{24}H_{34}Cl_6N_2PPt$	35.14 36.73	4.18 4.54	3.42 3.36	7.55 7.57	25.94[b] 24.86

[a]Impure. [b]Chloride. [c]Sulfur.

181-183°C. The analytical data are given in Table 6 and agree with the formula:



P-Phenyl-P,P-(diallyl)-aminophosphonium Hexachloroplatinate. P-phenyl-P,P-(diallyl)-aminophosphonium hexachloroplatinate was prepared in the usual manner by metathesis in the ethanolic solution. The melting point was 192-193°C. The analytical data given in Table 6 agree with the formula:



Attempted Preperation of the P-Phenyl-P,P-(diallyl)-aminophosphonium Picrate. On mixing the ethanolic solution of the aminophosphonium chloride and picric acid in ethanol a yellow colored turbidity appeared at once. A few oily droplets were noticed, possibly resulting from the hydrolysis of the aminophosphonium chloride to the phosphine oxide.

The Chloramination of Tris-(m-trifluoromethyl)-phosphine

The Preparation of the Tris-(m-trifluoromethyl)-phosphine. Tris-(m-trifluoromethyl)-phosphine was prepared for the first time because of the interest in the effect of having a trifluoromethyl group on the phenyl ring. The procedure employed in the preparation is described below:

To 24 grams (1.0 mole) of magnesium metal and 200 ml. of ether was added 123 grams (0.5 moles) of the m-trifluoromethylphenyl bromide during the course of three hours. To this Grignard reagent 23.0 grams (0.16 moles) of phosphorustrichloride in ether was added dropwise at about 0°C. The resulting product was treated with dilute hydrochloric acid. The ether layer was dried over Na_2SO_4 and after the removal of the ether was distilled under reduced pressure. The phosphine distilled over at 130-140°C./1 mm. as a viscous liquid; n^{25}_D 1.5210, d^{28} 1.3770. The analytical results confirm its identity.

Calcd. for
$(m\text{-}CF_3C_6H_4)_3P$: C, 54.00; H, 2.50; P, 6.65

Found: C, 53.75; H, 2.97; P, 6.35

Preparation of the Mercuric Chloride Adduct. The mercuric chloride adduct of the tris-(m-trifluoromethyl)-phosphine was prepared by mixing an ethanolic solution of mercuric chloride with the phosphine. The white crystalline product melted at 169-170°C.

Calcd. for
$(m\text{-}CF_3C_6H_4)_3P\text{-}HgCl_2$: C, 34.18; H, 1.64; Cl, 9.62

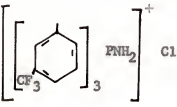
Found: C, 34.82; H, 1.93; Cl, 12.49

The Reaction with Chloramine. Into a solution of 16.05 grams (0.0364 mole) of tris-(m-trifluoromethyl)-phosphine in 40 ml. of ethyl ether, the gaseous mixture of chloramine and ammonia was bubbled in 30 minutes. The reaction tube was surrounded with an ice bath, thus keeping the reaction temperature between 0-5°C. Instantly, a cloudiness appeared, and after a few minutes a white precipitate separated out. The solid reaction product was filtered and washed with ether. The total solids weighed 10.4 grams after drying in the vacuum desiccator. From the filtrate and the washings, 8.6 grams of thick viscous liquid was isolated

after the removal of ether. This most probably is the starting material, along with some of the phosphine oxide.

The chloramination product was sparingly soluble in cold water but readily dissolved in hot water. It is also soluble in methanol and ethanol. The chloride analysis of this product showed 10.13 per cent of soluble chloride. Calculated for the formula $[(m\text{-}CF_3C_6H_4)_3PNH_2]^+Cl^-$: 6.85 per cent. This showed an impurity of approximately 10 per cent of ammonium chloride.

The product was freed from ammonium chloride by dissolving in hot chloroform. On filtration, white crystals separated out from the chloroform solution. The melting point was 214-215°C. The analytical results of these were in agreement with the formula:



Calcd. for $(m\text{-}CF_3C_6H_4)_3PNH_2Cl$: C, 48.71; H, 2.77; P, 5.98; N, 2.71; F, 33.03; Cl, 6.85

Found: C, 48.48; H, 2.85; P, 5.85; N, 2.92; F, 33.32; Cl, 8.26

The comparatively high analytical results for chlorine in the product could be due to the possible interference of the high percentage of fluorine present.

Attempted Preparation of Derivatives. On mixing the hot aqueous or ethanolic solution of the tris-(m-trifluoromethyl)-aminophosphonium

chloride with the ethanolic solution of the picric acid, no precipitate was obtained. On standing, oily droplets separated out from the mixture. Similar experiments with potassium hexafluorophosphate and sodium anthraquinone- -sulfonate did not give any crystalline derivatives.

Study of the Hydrolysis of the Aminophosphonium Chlorides. In order to confirm the structures of the aminophosphonium ions, several experiments on the hydrolysis were run. Tributylaminophosphonium chloride was chosen as the representative salt for these studies. These experiments showed that the decomposition takes place according to the following equation:

$$[(C_4H_9)_3PNH_2]^+Cl^- + H_2O \longrightarrow (C_4H_9)_3P{=}O + NH_4Cl$$

Identical results were obtained in water and in alkaline solution. Typical experiments for the aqueous and the alkaline hydrolysis are described below:

1) With water: 1.159 grams (4.6 mmoles) of P-tri-n-butylaminophosphonium chloride was treated with water and kept on a water bath for 50 hours, the temperature of the solution ranging between 60-70°C. The reaction mixture was extracted with ether. The distillate at 165-170°C./30 mm. gave an infrared spectrum compatible with that of an authentic sample of tri-n-butylphosphine oxide. Evaporation of the water phase gave 0.241 grams solid. The chloride analysis of this solid was 65.91 per cent, calculated for NH_4Cl, 66.29 per cent. The yield of NH_4Cl was quantitative.

2) With alkali: P-tri-n-butylaminophosphonium chloride 1.0574 grams (0.004 mole) in 25 ml. of NaOH was kept at room temperature for 48 hours. Following essentially the same procedure described in the

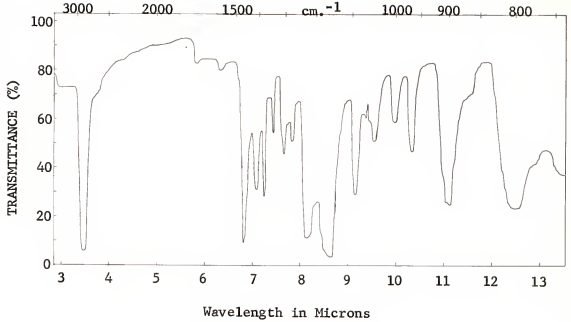


Fig. 2 Infrared Spectrum of Oxide from Hydrolyzed P-tri-n-butylaminophosphonium Chloride

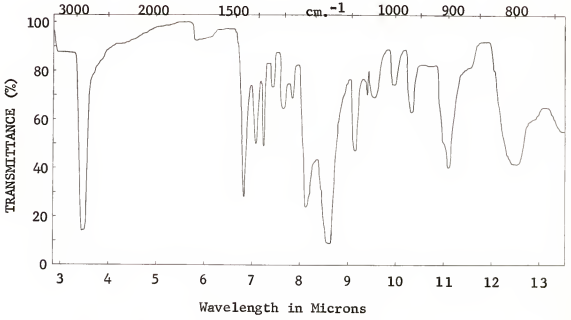


Fig. 3 Infrared Spectrum of Tri-n-butylphosphine Oxide

previous experiment, tri-n-butylphosphine oxide was isolated and identified. The ammonia contents in the aqueous layer were determined by the Kjeldahl method.

Found: 0.6994 grams. Calculated for NH_3: 0.7095 grams.

Discussion

The reaction of chloramine with the trisubstituted phosphines to form the trisubstituted aminophosphonium chlorides appears to be a general one. The results obtained are similar to the formation of 1,1,1-trisubstituted hydrazinium chlorides by the reaction of tertiary amines and chloramine.

These results indicate that the gas phase chloramination can be used for a variety of tertiary phosphines having aryl, alkyl, alkenyl, or cyclic hydrocarbon radicals substituted on the phosphorus atom. The presence of functional groups on the hydrocarbon radical does not necessarily interfere with the chloramination of the phosphine. This has been shown by the reaction of tris-(2-cyanoethyl)-phosphine and P-phenyl-P,P-(diallyl)-phosphine, where a nitrile and an olefinic group are incorporated in the molecule. The reactions of the phosphines with the chloramine are usually quantitative in nature. In some cases aminophosphonium chlorides were difficult to isolate in the pure state because of the presence of a small percentage of ammonium chloride, but their formation was fully established by the preparation of pure derivatives.

The solvent plays a role in these reactions. Non-polar solvents or solvents having low polarity give the best results. Ether was the choice in most of the cases except when the starting material was

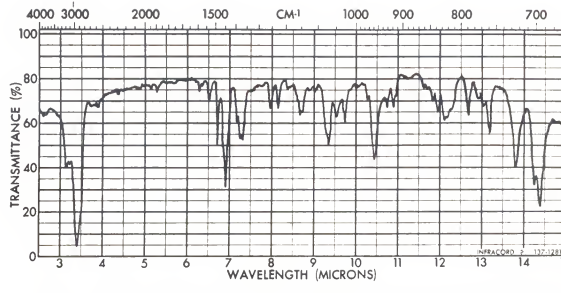


Fig. 4 Infrared Spectrum of P-tribenzylaminophosphonium Chloride

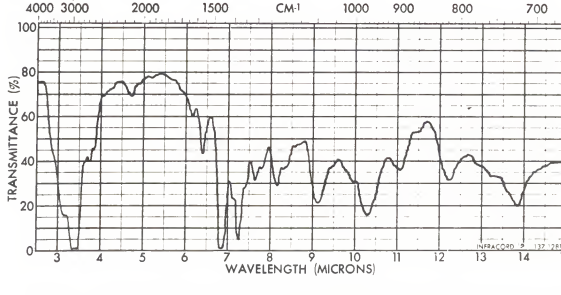


Fig. 5 Infrared Spectrum of P-tri-n-butylaminophosphonium Chloride

insoluble in it. The choice of the solvent was based on the consideration that the reaction product, an aminophosphonium chloride, because of probable ionic nature, would be less soluble in non-polar solvents, so that it would be precipitated, and thus removed from the reaction zone. This would avoid any further reaction with the chloramine, especially where the phosphine contained a functional group attached to one or more of its hydrocarbon radicals.

The structure of the aminophosphonium ion was suggested by the elemental analysis of the chlorides and the various stable derivatives. Further confirmation of the structure was obtained from the hydrolysis experiments. These experiments clearly show the cleavage of P-N bond in the molecule, to form the corresponding tertiary phosphine oxide.

The aminophosphonium salts have been classified as the quasi-phosphonium salts differing from the true phosphonium salts by having a P-N instead of one P-C linkage. The characteristic properties of these compounds indicate the probable ionic nature of bonding, but a penta-covalent arrangement about the phosphorus atom, however, cannot be completely ruled out. The aminophosphonium chlorides and their derivatives are crystalline solids, stable at room temperature. Although the exact structure of these compounds is not yet known, it is reasonable to assume sp^3 hydridization around the phosphorus atom. Some additional stability of the aminophosphonium ion could result from $d\pi$-$p\pi$ type of bonding, the unshared electron pair on the nitrogen donating to the empty d orbitals of the phosphorus atom, thus causing a more favorable charge distribution around P-N bond. This type of bonding would augment the σ type P→N coordinate bond already present in the ion.

$$\left[\geq P \leftarrow NH_2\right]^+$$

In this connection, it is very interesting to note that whereas triphenylphosphine reacts with chloramine to form the aminophosphonium chloride,[8,18] the corresponding hydrazinium chloride is not obtained by the reaction of triphenylamine with chloramine. Although triphenylamine is more basic than triphenylphosphine, the absence of $d\pi$-$p\pi$ type of bonding in the N-N linkage as compared with the P-N linkage, along with the steric effect of three phenyl groups around nitrogen atoms in the triphenylamine, could be the reasons for the instability of triphenylhydrazinium chloride.

The aminophosphonium chlorides are hydrolytically unstable. In aqueous, as well as in basic solutions, the aminophosphonium chlorides are quantitatively converted to corresponding phosphine oxides:

$$[R_3PNH_2]^+ + OH^- \longrightarrow R_3P{=}O + NH_3$$

The nucleophilic attack of the hydroxide ion on the phosphorus atom may be assumed to pass through an intermediate, finally to split off NH_3 and form the phosphine oxide.

$$[R_3PNH_2]^+ + OH^- \longrightarrow \left[R_3P\begin{matrix}\curvearrowright NH_2\\ \curvearrowright OH\end{matrix}\right] \longrightarrow R_3P{=}O + NH_3$$

The greater susceptibility of the aminophosphonium ion, $(R_3PNH_2)^+$, as compared to the hydrazinium ion $(R_3N\text{-}NH_2)^+$, to hydrolysis can be attributed to the presence of d orbitals in the phosphorus atom. This would facilitate the attack by the hydroxide ion.

Proposed Mechanism of the Tertiary Phosphine-Chloramine Reaction

During the course of this investigation, no kinetic studies were made to elucidate the mechanism of the reaction. Two different mechanisms for the chloramination reactions have been proposed in the literature. Audrieth and co-workers[23] and also Jander[24] have proposed the possible formation of chloramide ion, $NHCl^-$, or imine, NH, molecule in basic solutions. The formation of N_2H_4 from $ClNH_2$ and NH_3 is explained thus:

$$NH_2Cl + OH^- \longrightarrow NHCl^- + H_2O$$

$$NHCl^- \longrightarrow NH + Cl^-$$

$$NH + NH_3 \longrightarrow [NH_3NH] \xrightarrow{\text{Rearrangement}} N_2H_4$$

This mechanism is not applicable to these reactions, as they were carried out in non-aqueous solution in absence of any base.

The second mechanism proposed by Cahn and Powell[25] and later confirmed of Drago and Sisler[26] suggests the nucleophilic attack of the base, having a lone pair of electrons, on the chloramine molecule. For example, in the formation of hydrazine by ammonia and chloramine, a simple bimolecular displacement reaction takes place.

$$NH_3 + NH_2Cl \longrightarrow [H_3N\text{-}NH_2]^+ + Cl^-$$

In the presence of a base, a proton is removed from the hydrazinium ion, and hydrazine is set free.

$$[H_3N{:}NH_2]^+ + Cl^- + OH^- \longrightarrow H_2N\text{-}NH_2 + H_2O + Cl^-$$

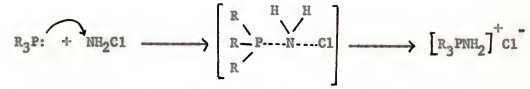
(or NH_3)

A similar mechanism has been proposed by Sisler and co-workers[6] for the formation of substituted hydrazines by the same reactions.

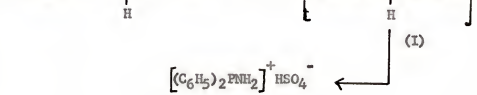
The formation of the proposed intermediate in the above reaction was confirmed by the preparation of 1,1,1-trisubstituted hydrazinium chlorides by Sisler and Omietanski.[7] In this case there is no available proton present on the base, hence, the reaction stops at the intermediate stages.

$$R_3N + NH_2Cl \longrightarrow [R_3N{:}NH_2Cl] \longrightarrow [R_3NNH_2]^+ + Cl^-$$

By analogy with the above results, it is believed that the tertiary phosphine-chloramine reaction also occurs through SN_2 mechanism (bimolecular displacement). In the Lewis acid-base sense, phosphines are strong bases due to the presence of a lone pair of electrons. This initiates a strong nucleophilic attack on the chloramine molecule.



Appel, Buchner and Guth,[17] in their studies of the formation of triphenylaminophosphonium hydrogen sulfate, $[(C_6H_5)_2PNH_2]^+HSO_4^-$, using triphenyl phosphine and hydroxylamine-O-sulfonate, proposed the following mechanism for the reaction.



The nucleophilic attack of hydroxylamine-O-sulfonate on the phosphine passes through an intermediate (I), which undergoes rearrangement to give the aminophosphonium salt.

This mechanism is not applicable to the chloramination of nitrogen bases. According to this mechanism, the intermediate requires the use of d orbitals, which are not available for bonding in case of nitrogen atom. In case of phosphorus atom where d orbitals are readily available, such intermediate formation cannot be ruled out. The initiation of the nucleophilic attack, however, is dependent on the nucleophilicity of the competing bases. No data are available to evaluate this factor.

CHAPTER II

STUDIES IN THE SYNTHESIS OF SUBSTITUTED PHOSPHONITRILIC POLYMERS

Introduction

Purpose of Investigation

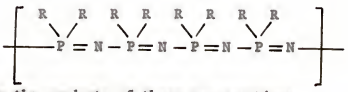
Modern technology demands materials resistant to high temperatures and which will retain their properties when continuously exposed to such conditions for a prolonged period of time. This has stimulated a tremendous amount of research in an effort to replace or modify the temperature-unstable, carbon-containing, organic polymeric systems by inorganic structures containing boron, silicon, or phosphorus together with oxygen and nitrogen.

It was Stokes[27] who first showed that when phosphonitrilic chlorides $(PNCl_2)_n$ are heated to temperatures above 300°C., they polymerize into rubber-like products. The so-called "inorganic rubber," however, exists in a metastable physical state and like elastomer sulfur reverts on standing to lower molecular weight products. The best known of the inorganic type of polymers so far, and also the most widely used, are the silicones. These polymers contain an inorganic backbone consisting of (SiO) units and find use as oils, greases, elastomers, hydraulic fluids, coatings, etc. The silicones are more stable to high temperatures than the corresponding carbon compounds, but are still inadequate for some needs. The silicon polymeric backbone is related to

the phosphonitrilic polymeric backbone in many ways. The PN and SiO groups are iso-electronic. Each group contains one element from the principal quantum number 3 and one from the principal quantum number 2. Both of these groups are known to form cyclic as well as linear polymers.

The two main purposes of this investigation were:

1) To find new paths to the synthesis of phosphonitrilic type of polymers when -PN- is the repeating unit and R is the alkyl or aryl group,



and to study the products of these new reactions.

2) To explore the possible application of chloramine as an oxidizing agent in these studies.

As one possible path for the formation of such polymers, the following type reactions were considered:

$$R_2PCl + 2NH_3 \longrightarrow R_2PNH_2 + NH_4Cl \qquad (i)$$

$$R_2PNH_2 \xrightarrow{(O)} R_2PN + H_2O \qquad (ii)$$

$$n\ R_2PN \longrightarrow (R_2PN)_n \qquad (ii)$$

Step (i) is the preparation of a disubstituted aminophosphine by the ammonolysis of a chlorophosphine. The aminophosphine could then be oxidized by using a mild oxidizing agent such as mercuric oxide, silver oxide, or oxygen in low concentrations. The di-substituted phosphonitrilic monomer thus obtained could then polymerize as in (iii).

The di-substituted aminophosphine could also react with chloramine to form the di-substitued phosphonitrilic monomer, through the elimination of one molecule of ammonium chloride.

$$R_2PNH_2 + NH_2Cl \longrightarrow \left[R_2P(NH_2)_2\right]^+Cl^-$$

$$\left[R_2P(NH_2)_2\right]^+Cl^- \xrightarrow{-NH_4Cl} \left[R_2PN\right]$$

The simplicity of the experimental procedure in the use of chloramine as an oxidizing agent was very encouraging. The exhaust gases of the chloramine generator, described earlier,[9] contain ammonia and chloramine. The large excess of ammonia over chloramine in these exhaust gases of the generator (the mole ratio of ammonia over chloramine is approximately 30:1) along with a very reactive group on the chlorophosphine should favor the ammonolysis-oxidation course for the reaction. That is, the ammonolysis,

$$R_2PCl + 2NH_3 \longrightarrow R_2PNH_2 + NH_4Cl$$

should proceed at a much faster rate than the chloramination of the phosphine,

$$R_2PCl + NH_2Cl \longrightarrow \left[\begin{matrix} & Cl & \\ R_2P & & \\ & NH_2 & \end{matrix}\right]^+ Cl^-$$

In this study the results obtained are those when the R group on the chlorophosphine are phenyl groups.

Historical Background

Liebig in 1834,[28] attempted to prepare amides of phosphoric acid by the reaction of ammonia and phosphorus pentachloride. Instead of the expected amides, he isolated a relatively small amount of a remarkably stable product, which could be steam distilled or boiled with acids and alkalies without undergoing appreciable decomposition. Gerhardt[29] and Laurent,[30] later showed that this product could be represented by the empirical formula $PNCl_2$. Gladstone and Holmes,[31] on the basis of vapor density measurement, proved the compound to be trimeric anc assigned to it the formula $(PNCl_2)_3$.

Some of the best work was done by Stokes,[27] at the turn of the century. In order to prevent the formation of completely ammoniated products, Stokes used ammonium chloride as a source of ammonia.

$$xPCl_5 + xNH_4Cl \longrightarrow (PNCl_2)_x + 4_xHCl$$

Many procedures and experimental techniques have been described in the literature.[32] Schenk and Romer,[33] improved Stokes' method by carrying out the above reaction in an autoclave, as well as in refluxing sym. tetrachloroethane. So far, the best results have been obtained by the procedure employed by Steinman, Schirmer, and Audrieth.[34] This procedure involves a controlled heating of the reactants in a long pyrex tube. A slight excess of ammonium chloride over the phosphorus pentachloride is required. The residue is extracted with low boiling petroleum ether. In all these reactions, monomeric or dimeric phosphonitrilic chlorides have not been isolated. The lowest member of the series obtained was the trimer, which comprised

40-45 per cent of the total. The tetramer amounted to 15-20 per cent of the product; the pentamer, 15-20 per cent; the hexamer, 1-3 per cent; and heptamer and higher members, about 25 per cent.

A comparable preparative method can be used for the phosphonitrilic bromides. The trimeric and tetrameric bromides $(PNBr_2)_{3,4}$ are prepared by the action of ammonium bromide on phosphorus pentabromide.[35,36] The phosphinitrilic fluorides do not result from the interaction of ammonium fluoride and phosphorus pentafluoride. They have been prepared by the fluorination of cyclic chlorides using potassium fluorosulfite.[37]

$$(PNCl_2)_4 + 8KSO_2F \longrightarrow (PNF_2)_4 + 8SO_2 + 8KCl$$

Cyclic trimeric and tetrameric fluorides have also been prepared by using silver fluoride as a fluorinating agent.[38] However, using lead fluoride gave mixed chlorofluorides.[39] Chapman and co-workers[40] have prepared phosphonitrilic fluorides $(PNF_2)_n$ for the range n=3 to n=11. They have given less detailed information for n=12 to 17. No phosphonitrilic iodides have thus far been prepared. The instability of the iodide could possibly result from steric effects.

Phosphonitrilic chlorides may be thought of as acid chlorides, and the reactions these substances undergo are similar to those of relatively stable acid chlorides. The phosphonitrilic chlorides undergo hydrolysis, esterification, react with ammonia, primary and secondary amines and many other donor molecules to form the substituted phosphonitriles. The number of partially or fully substituted derivatives of phosphonitrilic chlorides is very large and these have been summarized.[41]

Of the series of alkyl and aryl substituted phosphonitriles, realtively very little is known. Recently Searle[42] prepared the methyl substituted phosphonitriles by the reaction of dimethylphosphorus trichloride and ammonium chloride.

$$(CH_3)_2PCl_3 + NH_4Cl \longrightarrow [(CH_3)_2PN]_n + 4HCl$$

This reaction gives a very low yield of cyclic polymers, the chief product being a mixture of linear polymers. However, the latter have been successfully cyclized by refluxing them in chloroform with triethylamine and ammonium chloride. Yields of the order of 70-75 per cent of the trimer and tetramer have been obtained.

In the aromatic series, Rosset[43] prepared the fully phenylated cyclic trimer by the action of phenylmagnesium bromide on the trimeric chloride in boiling toluene. Partially phenylated trimers have also been prepared by Bode and Bach[44] by the Friedel-Craft reaction. Shaw and Stratton[45] prepared partially phenylated cyclic compounds by the reaction:

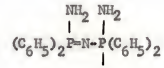
$$(C_6H_5)PCl_4 + NH_4Cl \longrightarrow [(C_6H_5)ClPN]_n + 4HCl$$

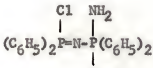
Bode and Thamer[46] reacted the tetrameric chloride with phenylmagnesium bromide to give partially and completely phenylated tetrameric products. Haber, Herring, and Lawton[47] prepared trimeric and tetrameric diphenylphosphonitriles by the reaction of diphenylphosphorus trichloride with ammonia and also with ammonium chloride.

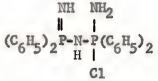
$$(C_6H_5)_2PCl_3 + 4NH_3 \longrightarrow [(C_6H_5)_2PN]_n + 3NH_4Cl$$

where n = 3,4.

Better results were obtained by the ammonia reaction in absence of a solvent. A moisture sensitive intermediate isolated in the above reactions was heated to 275°C. in vacuum to give 65 per cent over all yield of the phosphonitrile polymers. (n = 4, 48 per cent; n = 3, 7 per cent.) Bezman and Smalley[48] carried out the above reaction in chloroform. They isolated a stable intermediate in the reaction, for which they proposed the following possible structures:



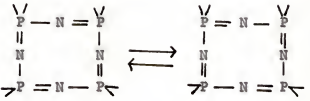




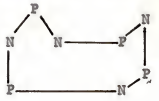
This intermediate on pyrolysis gave diphenylphosphonitrile polymers, from which was isolated predominantly the cyclic tetramer.

Structure: Brockway and Bright[49] studied the trimeric chloride $(PNCl_2)_3$ by electron diffraction. They found it to consist of a six-membered planar ring of alternate phosphorus and nitrogen atoms, with all bonds of equal length. The P-N bond length (1.65 ± 0.03Å) is much shorter than the value determined for a P-N single bond in sodium phosphoramidate (1.78Å). In addition, two chlorine atoms are bonded, one above and the other below the ring to each phosphorus atom. This gives the phosphorus atom a four co-ordinated structure, shaped somewhat like a distorted tetrahedron. A Kekule type resonance was postulated.

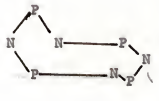
Ketelaar and de Vries[50] studied the tetramer $(PNCl_2)_4$ by X-ray diffraction. They found it to be an eight-membered ring, and, like the trimer, to have equal phosphorus-nitrogen bond lengths (1.67 ± 0.04Å). The crystal structure determination shows a significant difference from the trimer in that the ring is not flat but puckered. The spectroscopic evidence, however, indicates that it is flat in solution. The tetramer can be described in terms of the following resonance hybrids.



The ring structure of tetrameric fluoride is different, whereas in the tetrameric chloride crystal, the ring is boat shaped, in the fluoride it is in the chair form.



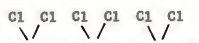
$P_4N_4Cl_4$ (crystal)



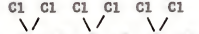
$P_4N_4F_8$ (crystal)

The fully phenylated derivative $(PNPh_2)_4$ exists in two forms, which may be related to each other in the same way as chloride and fluoride.

There is no certain knowledge of the structure of the higher polymers of the type $(PNCl_2)_n$ where n = 5 or greater. Cyclic structures of these polymers seem more likely for relatively small values of n. If the linear structures are postulated, the difficulty is what to do with the spare valencies on the terminal atoms. The following formulas represent two possibilities. Structure (a) is a diradical while (b) is highly polar.



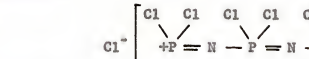
(a)



(b)

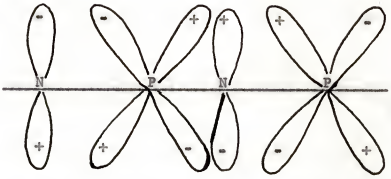
There is, however, no sign of behavior as diradical, nor do these substances have marked polar properties. The continuity of so many properties with those of the trimer and tetramer is in fact the strongest reason for believing that these larger molecules may be cyclic too. The fluoride series appears to be equally extensive. Chapman, et al.,[40] on the basis of vapor-phase chromatography and infrared absorption studies, has suggested the cyclic nature of phosphonitrilic fluorides up to $(PNF_2)_{17}$, with a thirty-four-membered ring. The existence of such large stable rings seems less unreasonable since the isolation of cyclic dimethyl siloxone series $\left[(CH_3)_2SiO\right]_n$ up to n = 9 which have an eighteen-membered ring.

These evidences are strengthened by the preparation of linear compounds of phosphonitrilic series $(PNCl_2)_nPCl_5$ from the cyclic trimer or tetramer.



These polymers have properties quite different from the cyclic ones.

The basis of aromatic character which is encountered in the phosphonitrile series is different from those in benzene or borazole, where the π bonding system is made up of p-orbitals. If we assume a sp^2 hybrid orbitals on nitrogen, one in each bond to phosphorus atom, two in a lone pair, then the fifth electron uses a p_z orbital for the formation of a π bond. Again, if we assume sp^3 hybridization on the phosphorus atom for the formation of four σ-bonds, it leaves an electron in d-orbital for π bonding. Thus the π bond formed between phosphorus and nitrogen is $d\pi$-$p\pi$ in nature. Craig[51] has pointed out that for symmetry reasons (for a $d\pi$-$p\pi$ system) complete matching is possible all around the ring which is formed with $(PN)_2$ units, as shown in the diagram:



Dig.: The formation of π-orbital from mixed p-d orbitals

Since tetrameric phosphonitrilic compounds are formed of $(PN)_2$ units, a stability greater than that of trimeric compound is to be expected.

Molecular orbital treatment of the π-electrons in the phosphonitrilic series by Craig and Paddock,[52] show that the symmetry properties have a deeper significance. In this series they require the highest filled orbital to be nondegenerate, as compared with benzene where the highest filled orbitals are degenerate.

Dig.: Energy sequences of the molecular orbitals, placed in an arbitrary energy scale

Accordingly, aromatic character is exhibited by benzene where four electrons are available to form a closed shell. Cyclo-octatetraen, the next in the carbon series is not aromatic in character. This is because the π-system constructed wholly of p-electrons form a closed shell for only $4n + 2$ pi electrons ($n = 1,2,3....$). In cyclo-octatetraen only two electrons are provided in the highest filled level while four electrons are required for shell closure. Next compound in the carbon series having ten pi electrons shall be aromatic in nature because four electrons are present in the highest filled level. The highest filled orbital of the phosphonitrilic series is always nondegenerate, so that even numbers of electrons complete a shell. This explains the aromatic character in all the members of phosphonitrilic series.

Materials

During the early phases of this research, diphenylchlorophosphine was prepared by the modified procedure of Gilman and Brown.[53] Later on the phosphine was commercially available from Victor Chemicals. The chloramine and ammonia mixture was obtained from the chloramine generator as described earlier in Chapter I.[9] All chemicals used were reagent grade.

Unless otherwise mentioned, the microanalyses were done by Galbraith Laboratories, Knoxville, Tennessee. All melting points are uncorrected.

Experimental and Results

Preparation of Diphenylchlorophosphine. Diphenylchlorophosphine was prepared by the thermal disproportionation of phenyldichlorophosphine in triphenylphosphine:

$$2C_6H_5PCl_2 \xrightarrow{(C_6H_5)_3P} (C_6H_5)_2PCl + PCl_3$$

The method used is a modification of the procedures described by Gilman and Brown.[53]

In a representative experiment, a mixture of 52.0 grams (0.2 mole) of triphenylphosphine and 40.0 grams (0.22 mole) of phenyldichlorophosphine was heated at 280-300°C. for 24 hours under an atmosphere of nitrogen. The reaction products were then fractionated under reduced pressure in a nitrogen atmosphere. Diphenylchlorophosphine (18.0 grams) was collected at boiling point 126°C./1.0 mm.; n_D 21.5°C.; 1.6338

(reported n_D 20°C.; 1.6340); yields as high as 70 per cent have been obtained by this method. The yield reported in the literature is only 29.5 per cent.

Preparation of Diphenylaminophosphine. The preparation of diphenylaminophosphine was attempted through various synthetic routes. Although the synthesis seems to be a straightforward one by the following equation:

$$(C_6H_5)_2PCl + 2NH_3 \longrightarrow (C_6H_5)_2PNH_2 + NH_4Cl$$

in no instance was an analytical pure sample of the diphenylaminophosphine obtained. The ammonolysis of the diphenylchlorophosphine was carried out in three different ways:

1) Ammonolysis in an organic solvent,

2) Ammonolysis in liquid ammonia,

3) Ammonolysis in the closed system reactions.

Among these, better results were obtained by procedures (1) and (3) than by procedure (2). Except for the low nitrogen analysis, the analytical results obtained were in fair agreement with the formula $(C_6H_5)_2PNH_2$. In the case of liquid ammonia, the course of the reaction seemed to be complicated, and the products formed could not be identified.

In addition to these ammonolysis reaction, the following methods were also employed to prepare diphenylaminophosphine,

$$(C_6H_5)_2PNa + NH_2Cl \longrightarrow (C_6H_5)_2PNH_2 + NaCl$$

$$(C_6H_5)_2PCl + NH_4Cl \longrightarrow (C_6H_5)_2PNH_2 + 2HCl$$

In the first reaction, whereas the end products of the reaction indicate that the reaction has taken place as per the equation, pure aminophosphine

could not be obtained. Moreover, this does not seem to be of practical use, as the over-all yield was very low.

The second reaction was carried out at high temperatures in absence of any solvent. From the reaction products a small percentage of diphenylphosphonitrilic cyclic tetramer was obtained. The possible source of oxidation seems to be traces of oxygen in the nitrogen gas used in the reaction.

Ammonolysis of Diphenylchlorophosphine in Chloroform. Chloroform used in these experiments was freed from ethanol by treatment with concentrated H_2SO_4 and redistillation. In a typical reaction diphenylchlorophosphine (10.55 grams) in 30 ml. of dry chloroform was added dropwise, with constant stirring, to a mixture of 75 ml. of liquid ammonia and 100 ml. of dry chloroform at -50 to -60°C. during a period of two hours. The excess ammonia was evaporated in a stream of nitrogen and the reaction flask, with contents, was transferred to a nitrogen-filled dry box. The reaction product was treated with dry chloroform and filtered. The resulting solid was analyzed and found to be essentially ammonium chloride (ca. 2.5 grams; near quantitative yield). Calcd. for NH_4Cl: Cl, 66.29 per cent

Found: Cl, 66.1 per cent

The chloroform-soluble fraction yielded a yellow-tinged solid on evaporation of the solvent. It melted over a range of 120-135°C. Attempts to crystallize the crude product from the usual hydrocarbon solvents failed. A sample for microanalysis was obtained by crystallization from chloroform, melting point was 130-135°C.

Calcd. for $(C_6H_5)_2PNH_2$: C, 71.65; H, 5.96; N, 6.97; P, 15.40

Found: C, 70.97; H, 5.43; N, 4.33; P, 13.09

Numerous attempts to prepare a stable derivative of the chloroform soluble product failed. For example, the addition of picric acid to a benzene or chloroform solution of the isolated product gave an intense orange coloration but no solid product separated out.

Ammonolysis of Diphenylchlorophosphine in Liquid Ammonia. Several reactions were carried out using liquid ammonia as a solvent for the ammonolysis of the diphenylchlorophosphine. In thes experiments, liquid ammonia was distilled in a three necked flask, fitted with a stirrer, a gas inlet and a dropping funnel. The phosphine was added without any solvent, dropwise, while the liquid ammonia was surrounded by dru ice-acetone bath kept at -70 to -75°C. Throughout the course of the reaction, dry nitrogen gas was passed through the system, so as to maintain a positive pressure of about 10-15 cm. of mercury. At the end of the run, dry nitrogen gas was used in siphoning the liquid ammonia to another flask. A typical reaction is described below:

Diphenylchlorophosphine was added to liquid ammonia under an inert atmostphere, with constant stirring at -70 to -75°C. To remove the ammonium chloride formed, its preferential solubility in liquid ammonia was employed. The supernatant ammonia solution was siphoned from the reaction flask, leaving the insoluble solid in the flask. This white solid was washed twice with fresh amounts of liquid ammonia. In one of the reactions 14.68 grams (0.0665 mole) of diphenylchlorophosphine was used. From the filtration and washings after the evaporation of the liquid ammonia, 3.50 grams of solid was recovered. This solid

contained 55.00 per cent chloride. Calculated for ammonium chloride: 66.29 per cent chloride.

The ammonia-insoluble portion was a white solid at the boiling point of liquid ammonia, but as the temperature was slowly raised to room temperature, still under an inert atmosphere, the white solid began to decompose with the evolution of a gas. After a time a dirty white viscous liquid remained in the reaction flask. Attempts to distill this product under vacuum failed.

Ammonolysis in Closed System. The high vacuum closed system used in these experiments is shown in the Figure 6. In the closed system, diphenylaminophosphine could not be obtained by the direct combination of diphenylchlorophosphine and ammonia in absence of any solvent medium. In these reactions diphenylchlorophosphine was introduced into the closed system, and while it was kept at liquid-air temperature, the entire system was evacuated. A slight excess over the stoichiometric amount of ammonia was condensed over the diphenylchlorophosphine at liquid-air temperature. The system was once again evacuated. The reaction flask was gradually brought to room temperature, and the excess of ammonia allowed to escape through the mercury bubbler. A white solid was left behind in the reaction flask. All efforts to distill this product under high vacuum at room temperature and also at elevated temperatures up to 200°C. failed. Only small amounts of ammonium chloride seemed to sublime under high temperature conditions.

Several ammonolyses of diphenylchlorophosphine in chloroform as solvent were carried out in the closed system. The reagent grade chloroform was first treated with concentrated sulfuric acid to remove the alcohol present and was then washed with water, dried over potassium

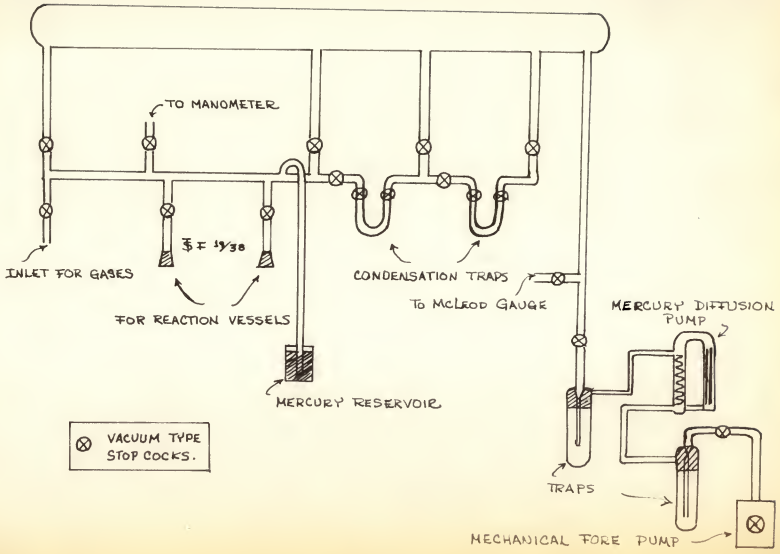
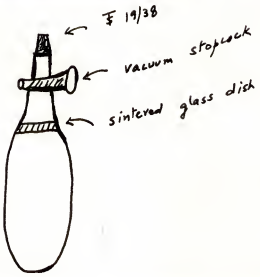


Fig. 6 High Vacuum Closed System

carbonate and distilled. The reaction tube used in these reactions was constructed as shown in the following diagram:



The reaction tube was attached to the closed system by a glass joint. Sintered glass was used in order to filter the ammonium chloride formed in the reaction. The choice of this solvent also depended upon its non-oxygenated nature, its polarity, and its low boiling point.

In a typical reaction 5.90 grams of diphenylchlorophosphine (0.027 mole) in 40 ml. of chloroform was transferred to the above described reaction tube in the nitrogen filled dry box. The reaction tube was then attached to the closed system, and while it was kept at liquid air temperature, the entire system was evacuated. An excess of ammonia was then introduced into the reaction tube at that temperature. While reaction products remained frozen, the system was evacuated. The reactants were then slowly brought to room temperature in this closed system.

The excess of ammonia escaped through the mercury bubbler. The reaction tube was removed from the system after closing the vacuum-type stopcock. The reaction products were filtered into a previously

evacuated tube in the system. After the solvent chloroform distilled off, a white solid remained in the bottom of the tube. This tube was sealed and the product sent for analysis. Different samples were analyzed for phosphorus and nitrogen. The chloroform solution was further used for attempted preparation of methyl iodide and picrate derivatives of diphenylaminophosphine.

The analytical results for these samples were: N, 3.90; P, 5.49. Calculated for $(C_6H_5)_2PNH_2$: N, 6.97; P, 15.40.

The low P and N analyses were believed to result from mercury contamination of the product from the system during the separation.

After all the chloroform solution was used up, the solid remaining in the reaction tube was removed by dissolving it in water. On the removal of water from this solution, the completely dried solid weighed 1.56 grams and contained 60.00 per cent chloride. The theoretical amount of ammonium chloride calculated for the reaction is 1.43 grams. Hence, this solid is probably principally ammonium chloride.

In similar reactions 6.10 grams of diphenylchlorophosphine in 40 ml. of chloroform was used. All of the necessary precautions were taken to keep mercury out of the reaction tube. The chloroform-soluble product now gave the following analytical results:

Calcd. for $(C_6H_5)_2PNH_2$: C, 71.65; H, 5.96; N, 6.97; P, 15.40

Found: C, 72.19; H, 5.29; N, 4.53; P, 14.62

In another attempt to determine the total nitrogen contents of the final reaction products of diphenylchlorophosphine and ammonia, using chloroform as solvent medium, 2.95 grams of diphenylchlorophosphine in 100 ml. of chloroform was used. A similar procedure to that described previously was employed. After the reaction was complete the chloroform

was completely distilled. The residue was pumped for several hours in order to remove the traces of ammonia and chloroform from it. This residue was then analyzed for total nitrogen content.

Calcd. for a 1:1 molar mixture of
$(C_6H_5)_2PNH_2$ + NH_4Cl: N, 11.01

Found: N, 9.57

Attempted Preparation of Derivatives of Diphenylaminophosphine. The chloroform-soluble product obtained by the reaction of diphenylchlorophosphine and ammonia, as mentioned earlier, was used for the preparation of the methyl-iodide and picric-acid derivatives. Methyl iodide dissolved in chloroform was mixed with the above solution in a closed system. The solid thus obtained after the complete removal of chloroform and excess of methyl iodide did not melt but started decomposing above 290°C. The solid was analyzed for iodide. The high halogen content of this product was in reasonable agreement with the formation of an ammonia-methyliodide adduct.

By mixing the chloroform solution of picric acid and above mentioned reaction solution, a small amount of yellow precipitate was isolated from the deep orange solution. This did not melt up to 300°C. and could not be further crystallized from ethanol.

Reactions of Sodium Diphenylphosphide with Chloramine. In an attempt to synthesize diphenylaminophosphine, the gaseous chloramine from the chloramine generator was made to react with sodium diphenylphosphide.

$$(C_6H_5)_2PNa + NH_2Cl \longrightarrow (C_6H_5)_2PNH_2 + NaCl$$

Sodium diphenylphosphide was prepared by the method of Kuchen and Buchwald[54] by the reaction of diphenylchlorophosphine with

sodium metal in refluxing di-n-butylether. The yellow suspension of the sodium diphenylphosphide was reacted with chloramine gas, without

$$(C_6H_5)PCl + 2Na \longrightarrow (C_6H_5)_2PNa + NaCl$$

separating the sodium-chloride formed in the above reaction.

Several reactions were run and the products isolated in the nitrogen-filled dry box. A typical reaction is described below:

Diphenylchlorophosphine, 9.17 grams (0.0407 mole) was used to prepare the sodium salt in di-n-butylether. The resulting suspension was transferred to the reaction tube and chloramine from the generator was bubbled through this suspension for 45 minutes at room temperature. The yellow color slowly disappeared and a thick white precipitate settled out in the reaction tube. This was then transferred to the nitrogen-filled dry box, and the reaction products were filtered. The solid obtained was treated with sodium-dried benzene at 60°C. The filtrate, after the complete removal of di-n-butylether, gave a small amount of resinous product. The benzene soluble product was a solid (about 0.5 grams) which melted at 149-151°C. Complete removal of benzene after filtration gave a semi-solid residue. The benzene-soluble solid was completely analyzed.

Calcd. for $(C_6H_5)_2PNH_2$: C, 71.65; H, 5.96; P, 15.40; N, 6.97; Mol. Wt., 201.19

Cacld. for $(C_6H_5)_2\overset{O}{\uparrow}PNH_2$: C, 66.30; H, 5.54; P, 14.28; N, 6.45; Mol. Wt., 217.9

Found: C, 67.14; H, 6.18; P, 13.87; N, 6.08; Mol. Wt., 272.0

(Rast method)

The infrared spectrum of this product in Nujol shows absorption bands at 3150 cm.$^{-1}$ and 3270 cm.$^{-1}$ corresponding to monosubstituted phenyl and N-H stretching. The absorption at 1180 cm.$^{-1}$ corresponds to P→O. The acid hydrolysis of this compound gave a product melting at 187-189°C., the infrared absorption spectra of which was identical with that of diphenylphosphinic acid.

$$(C_6H_5)_2\overset{\uparrow O}{P}NH_2 + H_2O \longrightarrow (C_6H_5)_2\overset{\uparrow O}{P}\text{-}OH + NH_3$$

The data indicate the probable formation of a mixture of diphenylaminophosphine oxide and diphenylaminophosphine from the reaction of sodium diphenylphosphide and chloramine. The most probable source of oxidation of diphenylaminophosphine seems to be in the traces of oxygen in the system. The yield of the solid isolated from benzene was very poor.

Reaction of Diphenylchlorophosphine with Ammonium Chloride. The reaction of diphenylchlorophosphine with ammonium chloride to provide diphenylaminophosphine was investigated.

$$(C_6H_5)_2PCl + NH_4Cl \longrightarrow (C_6H_5)_2PNH_2 + 2HCl$$

In a typical experiment a mixture of 12.29 grams (0.056 mole) of diphenylchlorophosphine and 2.98 grams (0.056 mole) of ammonium chloride was heated under a nitrogen atmosphere at temperature ranging from 260-270°C. for eight hours. The reaction flask with its contents was then transferred to a dry box. The reaction provided two distinct products.

1) A white hygroscopic sublimate, which adhered to the cooler portions of the reaction flask; it was soluble in most common organic solvents.

2) A hard residue remaining in the bottom of the flask. This product was almost completely soluble in hot benzene. The insoluble portion was identified as unreacted ammonium chloride. From the benzene solution white needle shaped crystals were obtained which melted at 310°C. Recrystallization from benzene raised the melting point to 319-321°C. This compound was identified as tetrameric diphenylphosphonitrile. The reported melting point was 319-321°C.[47] The elementary analysis conforms to the formula $\left[(C_6H_5)_2P\ N\right]_4$.

Calcd. for $C_{48}H_{40}P_4N_4$: C, 72.3; H, 5.1; P, 15.6; N, 7.0

Found: C, 71.9; H, 5.3; P, 15.4; N, 7.0

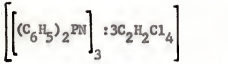
The yield of the tetramer on the basis of several experiments was 10-12 per cent. The possible oxidizing agent in these reactions could be the trace amount of oxygen present in the nitrogen gas employed for the reactions.

$$(C_6H_5)_2PNH_2 \xrightarrow{(O)} \left[(C_6H_5)_2PN\right]_n$$

Reaction of Diphenylchlorophosphine with a Gaseous Mixture of Ammonia and Chloramine. It was mentioned earlier that one of the possible paths for the formation of phosphonitrilic polymers is simultaneous ammonolysis and chloramination of diphenylchlorophosphine. Accordingly a large number of experiments were performed, where diphenylchlorophosphine in sym. tetrachloroethane solution (boiling range 144-150°C.) was treated with a gaseous mixture of ammonia and chloramine, from the chloramine generator described in Chapter I.[9]

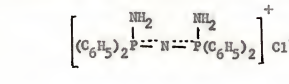
From the reaction products obtained in this reaction, two distinct compounds were isolated and identified. The compound melting at 114°C.

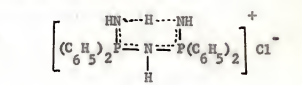
was identified as an adduct of cyclic diphenylphosphonitrile trimer, and three molecules of tetrachloroethane (hereafter referred to as compound I).



Compound I

The second compound isolated from the reaction products was identified and represented by the following two structures:





(hereafter referred to as compound II). An analytical pure sample of compound II melted at 240°C. Below are described two of the typical reactions of the diphenylchlorophosphine with ammonia and chloramine.

Reaction 1. The effluent gases from the chloramine generator were bubbled through a solution of 8.0 grams of diphenylchlorophosphine (0.04 mole), in 90 ml. of sym.-tetrachloroethane, for 30 minutes (approximately 0.05 mole of chloramine and a large excess of ammonia). The reaction tube was externally heated with an infrared lamp. Immediate precipitation occurred on passage of the gases. After a few minutes from the start of the reaction, the temperature rose to the reflux temperature of the solvent. As the reaction proceeded, the reaction mixture slowly assumed light yellow color. The temperature dropped slowly and remained between 80-90°C. during the remaining part of the reaction.

At the end of the run, the reaction products were transferred to a semi-micro filtration assembly where they were filtered under moisture-free conditions. The solid was washed with two 50 ml. portions of tetrachloroethane. The filtrate and the washings were combined and the volume of solvent was reduced to about 15-20 ml. under reduced pressure. Upon filtration 4.2 grams of solid was isolated (melting point was 230-234°C.; yield was 51 per cent based on diphenylchlorophosphine used). This solid on recrystallization from methanol melted at 240°C. This is identified as compound II in the following discussion. The analytical data for this compound are given in Table 8. On addition of ether to the filtrate, a yellowish colored solid melting at 215-220°C. separated out (0.75 gram). The infrared spectrum of this solid was comparable with compound II. After the complete removal of the solvent, a brownish resinous material was obtained.

The solids obtained in the above reaction were treated with three 50 ml. portions of boiling benzene. The volume of this benzene solution was reduced to about 40 ml. On standing, white needle-shaped crystals separated out. The crystals were filtered and weighed (0.85 gram). A second crop of crystals from the same solution was obtained (0.45 gram). The total weight was 1.3 grams. Both of these melted at 113-114°C. This product is identified as compound I in the discussion which follows (yield 10 per cent).

Reaction 2. In this reaction 11.50 grams of diphenylchlorophosphine (0.052 mole) in 90 ml. of tetrachloroethane was used. The chloramine and ammonia mixture was bubbled in for 35 minutes. The procedure was identical with that in reaction 1. From the tetrachloroethane 5.6 grams

of solid melting at 228-232°C. was obtained (yield 47.5 per cent). The ether-insoluble solid weighed 0.85 gram and melted at 210-214°C. From the benzene solution, a total of 3.4 grams of compound I was obtained (yield 18 per cent).

A summary of the results of five reactions is shown in Table 7.

Compound I

1) Analysis. The elemental analysis of compound I is given below. The sample used for these analyses were from two different reactions. The analysis is in agreement with the empirical formula of this compound, $C_{42}H_{36}N_3P_3Cl_{12}$.

Calcd. for $C_{42}H_{36}N_3P_3Cl_{12}$: C, 45.80; H, 3.29; P, 8.43; N, 3.81; Cl, 38.64

Found: Sample I: C, 46.14; H, 3.51; P, 8.84; N, 4.39; Cl, 37.52

Sample II: C, 46.68; H, 3.47; P, 8.58; N, 4.46

2) Melting Point. Compound I on slow crystallization from benzene solution is obtained in shining, needle-shaped crystals. It has a good storage life if kept in a tightly stoppered bottle. On exposing these crystals to atmosphere for a few hours, they lose their luster and slowly decompose to give a powdery mass. A similar result is obtained when these crystals are pumped on in a desiccator for some time.

The compound melts sharply at 113-114°C. On increasing the temperature slowly, bubbles arise from the molten mass in the melting point tube, when the bath temperature is 140°C. to 150°C. When all the bubbles have escaped, the molten mass in the melting point tube becomes solid once again. The second melting point occurs at 226-228°C.

3) Decomposition of Compound I. In an experiment, 0.8170 grams of compound I was pumped on in a desiccator at a pressure of 0.2 mm. for

TABLE 7

A Summary of Reactions of Diphenylchlorophosphine-Ammonia and Chloramine

Reaction No.	Amount of Phosphine Grams	Moles of Phosphine	Solvent ml.	App. Moles of NH_2Cl	Yield Compound I		Yield Compound II	
					Grams	Per cent	Grams	Per cent
1	8.00	0.036	90	0.04	1.6	12	4.1	50
2	8.00	0.036	90	0.04	1.3	10	4.2	51
3	11.5	0.052	90	0.6	3.4	18	5.6	47.5
4	11.5	0.052	90	0.6	3.3	17	6.0	50
5	15.6	0.076	90	0.8	6.2	23	---	---

31 hours. The desiccator was kept warm by an infrared lamp. At the end of the run, the amorphous mass weighed 0.4449 gram and melted at 228-229°C. The infrared spectrum of this product was identical with an authentic sample of diphenylphosphonitrile trimer. The analytical results for this product are in agreement with theory for trimeric diphenylphosphonitrile.

Calcd. for $C_{36}H_{30}P_3N_3$: C, 72.15; H, 5.16; P, 7.43; N, 15.55; Mol. Wt., 598

Found: C, 72.46; H, 4.95; P, 7.29; N, 15.61; Mol. Wt., 571

Reported melting point of the cyclic trimer is 228°C.,[46] 230-232°C.[47]

The calculated amount from the formula of compound I gives 0.4433 gram of the trimer for this experiment, which is in fair agreement with 0.4449 gram obtained.

4) Formation of Compound I. A known sample of diphenylphosphonitrile cyclic trimer was dissolved in benzene. To this benzene solution tetrachloroethane was added. The mixture on standing overnight gave crystals which melted at 114-115°C. The infrared spectrum of this compound was identical with that of compound I. The mixed melting point with compound I showed no depression.

5) Hydrolysis: Base. In an experiment 0.630 gram of compound I was dissolved in 20 ml. of benzene and to this solution 10 ml. of 20 per cent NaOH was added. The mixture was refluxed for 15 hours. Benzene was distilled off and from the solution a white solid separated out. After drying, it weighed 0.353 gram and melted at 230°C. The infrared spectrum of this product was identical with the diphenylphosphonitrile cyclic trimer.

Acid

In one experiment, 0.750 gram of compound I was dissolved in 20 ml. of benzene and to this solution 10 ml. of dilute nitric acid was added. The mixture was refluxed for 15 hours. Benzene was distilled off and from the remaining solution, a white solid was obtained (0.476 gram). This solid after drying melted at 180-181°C. The spectrum of this product was identical with that of diphenylphosphinic acid (literature value of melting point).

6) Infrared Spectrum. The infrared spectrum of compound I is shown on page 68. It was run as a KBr pellet on a Perkin-Elmer Infracord Spectrophotometer using sodium chloride optics. The principal bands in the spectrum were:

3077w, 3103m, 1970w, 1477m, 1435s, 1274m, 1235w, 1190v.s., 1170s, 1120s, 1070w, 1028m(sh), 1000w, 855m, 800s, 785s, 755m, 738s, 722s, 696s.

The infrared spectrum of the trimeric diphenylphosphonitrile obtained after the removal of three molecules of the tetrachloroethane contained the following principal absorption bands:

3086m, 1961w, 1887w, 1818w, 1626w, 1587sh, 1481m, 1433s, 1374w, 1302w, 1235sh, 1190s, 1175s, 1120s, 1068m, 1030s, 1000m, 917w, 850m, 753m, 746sh, 720s, 693s.

Compound II

1) Analysis. This compound II was obtained from the tetrachloroethane solution. On recrystallization from methanol it melted at 240°C. On the basis of the elemental analysis of the compound shown in Table 7, its empirical formula is $C_{24}H_{24}P_2N_3Cl$. This compound is apparently identical with the intermediate isolated by Bezman and Smalley,[48] from

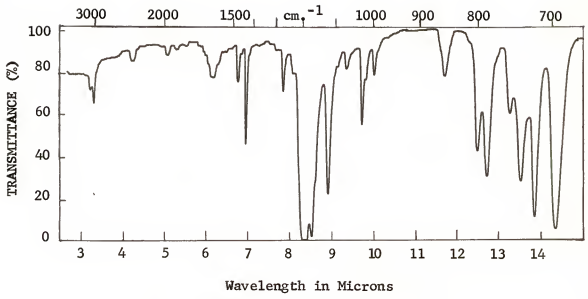


Fig. 7 Infrared Spectrum of Compound I

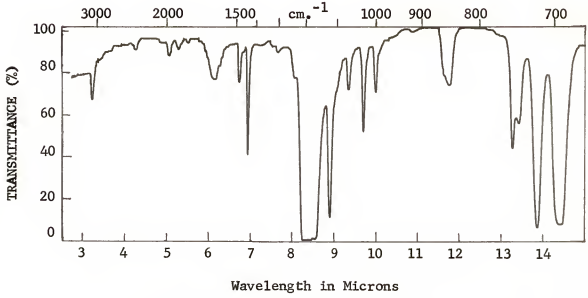


Fig. 8 Infrared Spectrum of Diphenylphosphonitrilic Trimer

the reaction of diphenylphosphorus trichloride with ammonia gas in chloroform solution. The infrared spectrum of the compound II was identical with one obtained by Bezman and Smalley for their intermediate and kindly supplied by Dr. Bezman for comparison (Figures 9 and 10).

Compound II is soluble in ethanol, methanol, acetone, chloroform and also sparingly soluble in cold water.

2) Derivatives of the Compound II. It was found that the chlorine in compound II could be replaced by simple metathetical reactions, by many complex negative ions such as picrate, hexafluorophosphate, and anthraquinone-β-sulfonate. This indicated a probable ionic nature of the chlorine present in the compound II.

The picrate derivative of compound II was prepared by mixing a hot aqueous solution of compound II with aqueous solution of picric acid. A precipitate was obtained immediately. The precipitate was filtered, and the solid recrystallized from an ethanol and water mixture. After drying the picrate melted at 147°C. The nitrogen analysis shown in Table 8 agrees with the theory.

The anthraquinone-β-sulfonate derivative of compound II was prepared by simple metathesis in aqueous solution. It was recrystallized in ethanol and water mixture. The melting point was 218°C. The nitrogen analysis of this derivative shown in Table 8 agrees with the theory.

The hexafluorophosphate derivative of compound II was prepared by mixing the aqueous solutions of compound II and potassium hexafluorophosphate. After crystallization in ethanol and water mixture, this derivative melted at 153-154°C. The nitrogen analysis shown in the Table 8 agrees with the theory.

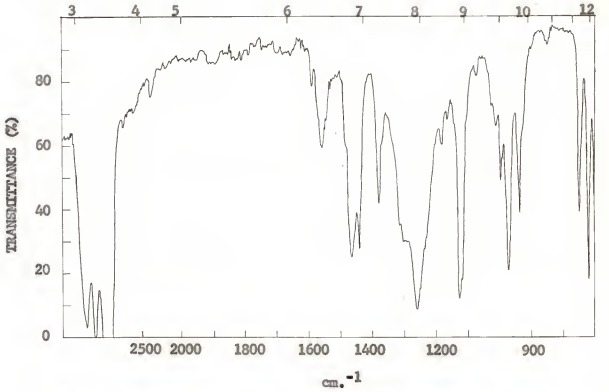


Fig. 9 Infrared Spectrum of the Intermediate Obtained by Bezman and Smalley from Diphenylphosphorus Trichloride-Ammonia Reaction

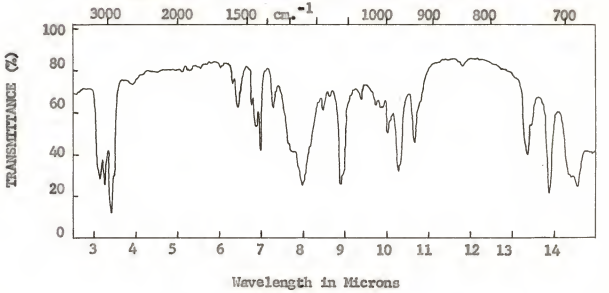


Fig. 10 Infrared Spectrum of Compound II

3) Infrared Spectrum of Compound II. The infrared absorption spectra of compound II was run as a Nujol mull on a Perkin-Elmer Infracord Spectrophotometer using sodium chloride optics. The spectrum in the far infrared region (between 15 and 38 microns) was run as a Nujol mull on a Perkin-Elmer 221 Spectrophotometer using cesium bromide optics.

The principal absorption bands in the spectrum of compound II and its hexafluorophosphate derivative are given below:

Compound II:

3185m, 3085m, 2941s, 2857sh, 1563w, 1548m, 1450m, 1440m, 1370m, 1294sh, 1250s, 1176w, 1160w, 1124s, 1114sh, 1068w, 1026w, 1010w, 996w, 971m, 936m, 845w, 746m, 719s, 694sh, 687s, 535m, 524broad, 503m, 444m, 418m.

Hexafluorophosphate Derivative of Compound II:

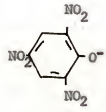
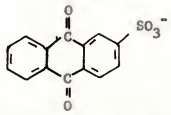
3508m, 3416m, 2941s, 2857sh, 1587w, 1550m, 1460s, 1439m, 1379m, 1250m, 1190w, 1124m, 1031w, 1000w, 976w, 840broad, 757sh, 741m, 721m, 687m, 559s, 543w, 501m, 476w, 418w.

4) Nuclear Magnetic Resonance Spectrum of Compound II. The nuclear magnetic resonance spectrum of compound II was run at 19.3 megacycles in a Varian high resolution spectrometer, in chloroform solution. A single peak for P^{31} was observed corresponding to a chemical shift of 20.3 p.p.m. to low field from external 85 per cent phosphoric acid reference.

5) Pyrolysis of Compound II. Three and twelve hundredths grams of the compound II was heated for three hours at 260-265°C. The dark colored residue was treated with 150 ml. of boiling benzene and filtered.

TABLE 8

$$\left[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2\right]^+ X^-$$

X^-	Melting Point °C.	Empirical Formula	Analyses								
			%C Calcd.	%C Found	%H Calcd.	%H Found	%P Calcd.	%P Found	%N Calcd.	%N Found	%Cl Calcd. / Found
Cl^-	240	$C_{24}H_{24}P_2N_3Cl$	63.78	63.75	5.53	4.98	13.71	13.60	9.30	9.41	7.85 / 8.50
PF_6^-	153-154	$C_{24}H_{24}N_3P_3F_6$	---		---		---		7.49	7.46	---
	147	$C_{30}H_{36}N_6P_2O_7$	---		---		---		13.04	12.83	---
	218	$C_{38}H_{31}N_3O_2SO_5$	---		---		---		5.97	5.82	---

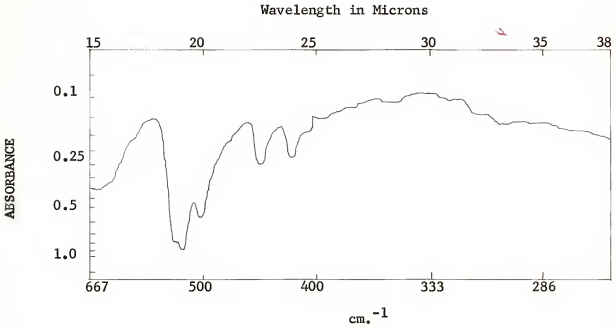


Fig. 11 Infrared Spectrum of Compound II

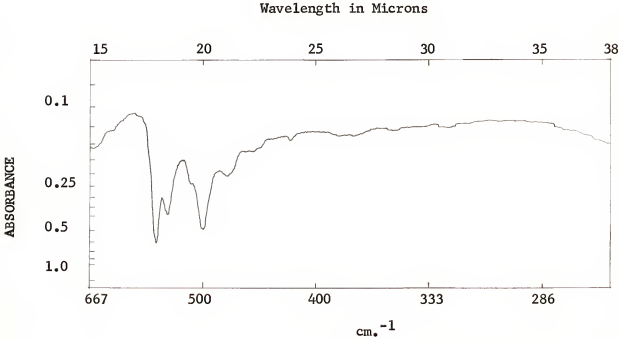


Fig. 12 Infrared Spectrum of Hexafluorophosphate Derivative of Compound II

The filtrate on reduction of volume gave 1.52 grams of solid melting at 315-316°C. The infrared sample of this solid was identical with an authentic sample of the diphenylphosphonitrile cyclic tetramer (literature value 310°C.[46], 319-321°C.[47]). The yield of the tetramer was 55.4 per cent based on compound II. On further reduction of the volume of benzene solution, 0.8 gram of solid melting at 226°C. was isolated. This was identified as cyclic trimer. The yield of the trimer was 29 per cent.

6) Chloroform Adduct of Compound II. Upon crystallization of the compound II in chloroform, the product isolated melted at 240°C. but the infrared spectrum of this product was not identical with that of the compound II, which was obtained from methanol. The chloroform product was found to be 1:1 adduct of compound II and chloroform molecule.

Calcd. for $C_{29}H_{24}P_2N_3Cl_4$: C, 52.56; H, 4.41; P, 10.85; N, 7.36; Cl, 24.83

Found: C, 52.46; H, 4.14; P, 11.15; N, 6.77; Cl, 24.60

This adduct can be converted to compound II either on crystallization in methanol or heating the product under the vacuum.

Discussion

Various attempts were made to synthesize diphenylaminophosphine through different synthetic routes. In no instance was an analytically pure sample of this compound obtained. Except for the reaction involving ammonolysis of diphenylchlorophosphine in liquid ammonia, all other methods gave impure diphenylaminophosphine. The carbon, hydrogen, and phosphorus analysis of these products agreed fairly well with the theory,

but the nitrogen analysis was found always to be low. The best results were obtained in closed system reactions and ammonolysis in chloroform as a solvent.

From the reaction of diphenylchlorophosphine with gaseous ammonia and chloramine, in sym.-tetrachloroethane, two distinct products were isolated and identified.

The chemical and physical evidence obtained from the compound I, was in agreement with the formula assigned to this compound, an adduct of diphenylphosphonitrile cyclic trimer and three molecules of tetrachloroethane.

$$\left[\left[(C_6H_5)_2PN\right]_3 : 3C_2H_2Cl_4\right]$$

A very high degree of stability is exhibited by the phosphonitrilic ring system of compounds. They are either chemically inert or react very slowly. Therefore, we would not expect compound I to be a very stable species. This was found to be the case. Compound I loses tetrachloroethane molecules slowly when exposed to the atmosphere. The removal of these solvent molecules, however, could be accelerated when the compound was pumped under reduced pressure. This property suggests rather weak binding forces between the cyclic trimer and the tetrachloroethane molecules.

It is believed that compound I is a molecular addition compound formed through electron pair donor-acceptor interaction. It is probable that the lone electron pair on the nitrogen atom in the phosphonitrilic ring might act as an extremely weak base towards the tetrachloroethane molecule. It is equally probable that the phosphonitrilic

trimer is acting an electron acceptor through the chlorine atoms in the tetrachloroethane molecule.

It is known that the phosphorus nitrogen ring in the phosphonitrilic chloride cyclic trimer is planar, and each pair of chlorine atoms are placed as one chlorine atom above and one below the plane of the ring. It can be assumed by analogy that the P-N ring in diphenylphosphonitrile cyclic trimer is also planar and each pair of phenyl groups are placed one phenyl above and one below the plane of the ring. It is quite possible that the spatial orientation of the two phenyl groups is such that they are able to "envelope" or "sandwich" or "trap" between them, one molecule of tetrachloroethane, which happens to be present when the crystals of the trimer are being formed.

In the absence of any structural determination studies, the nature of attachment of the solvent molecules to the cyclic trimer is only speculative. There is, however, some reference to the formation of such addition type of compounds between tertiary amines and the phosphonitrilic chlorides.[32] These compounds are, however, very poorly characterized. The more definite addition compound isolated by Bode and Bach,[44] was formulated as $(PNCl_2)_3{:}2AlCl_3$, where the attachment of the $AlCl_3$ molecules were shown to be on the chlorine atoms.

The infrared absorption spectra of compound I shows a strong absorption at 1190 $cm.^{-1}$. This corresponds to P=N absorption characteristic ring vibration frequency. The "ring elongation" frequency referred by Daasch[55] in the phosphonitrilic chloride cyclic trimer was at 885 $cm.^{-1}$. Compound I shows a medium absorption peak at 855 $cm.^{-1}$ corresponding to such type of absorption. Below are tabulated some of the known "characteristic ring vibrations" of phosphonitrilic derivatives.

Compound	Ring Vibration in cm.$^{-1}$		Reference
$(PNF_2)_3$	1305	975	56
$(PNCl_2)_3$	1218, 1201	885	55
$(PNBr_2)_3$	1184	---	57
$(PN(CH_3)_2)_3$	1180	---	42
Found: Compound I	1190, 1170	855	--

The trend of the ring vibration frequency is gradual and shows an increase of frequency as the substituent on phosphorus atom became increasingly electronegative. Shaw,[57] tabulated the characterized ring vibration of a large number of phosphonitrilic derivatives, and suggested the use of this characteristic absorption in determining the size of the phosphonitrilic ring in these compounds. The appearance of these absorption peaks in the spectrum of compound I shows the presence of trimeric species in the molecule.

In addition to other usual absorption bands in the spectrum of compound I, there are three additional absorption peaks which are absent in the spectrum of cyclic trimer. These are at 1274, 800, and 785 cm.$^{-1}$. In the spectrum of tetrachloroethane there is a corresponding absorption at 1274 cm.$^{-1}$. However, the broad C-Cl absorption band in the tetrachloroethane molecule between 785 and 810 cm.$^{-1}$ seems to have split into two sharp peaks in the spectrum of compound I. This splitting might suggest a possible attachment of one chlorine atom in the tetrachloroethane molecule with the phosphonitrilic ring, thus giving two types of C-Cl stretching vibrations.

The final proof for the structure of compound I as being 1:3 adduct instead of 1:1 with diphenylphosphonitrile and tetrachloroethane, was obtained by the formation of this compound from a known sample of cyclic trimer and tetrachloroethane in benzene solution. Because of the high stability of the phosphonitrilic ring, energy considerations alone should rule out its possible dissociation to monomers and formation of 1:1 adduct.

The structure of compound II was established by its elemental analysis, infrared spectrum studies, nuclear magnetic resonance studies and the analysis of its derivatives prepared by the replacement of chlorine by various complex anions.

In the infrared spectrum of compound II, P=N absorption was identified at 1250 $cm.^{-1}$. This absorption frequency is somewhat higher than the P=N absorption in ring compounds or P=N absorption in phosphinimines, reported by Horner and Oediger,[16] at 1180 and 1160 $cm.^{-1}$. This could possibly be the result of the increased force constant of P-N bond resulting from the presence of a positively charged phosphorus atom in the molecule. Two medium absorption peaks at 3185 and 3085 $cm.^{-1}$ were assigned to monosubstituted phenyl and N-H stretching vibrations. The spectrum also contains two bands at 936 and 971 $cm.^{-1}$ which may indicate P-N-P grouping in the molecule.

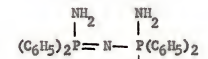
The infrared spectrum of the hexafluorophosphate derivatives of compound II, shows a monosubstituted phenyl and N-H stretching vibration to 3508 and 3416 $cm.^{-1}$. The P=N occurs at the same place, 1250 $cm.^{-1}$. The P-F stretching vibration occurs at 840 $cm.^{-1}$ as reported by Buhler and Bues.(58)

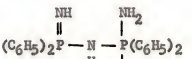
In the far infrared spectrum of the compounds II and its hexafluorophosphate derivative, a strong broad absorption band averaging at 524 cm.$^{-1}$ appears in the spectrum of compound II. This absorption is comparable to the reported values of P-Cl by Daash and Smith.[59]

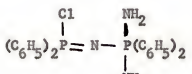
This absorption band is not present in the hexafluorophosphate derivative. The medium absorption peak at 559 cm.$^{-1}$ present in the hexafluorophosphate derivative was identified as the F-P-F bending vibration in the hexafluorophosphate ion. The reported value for such bending vibration by Buhler and Bues is at 555 cm.$^{-1}$.

These infrared data suggest the possibility of a P-Cl covalent linkage in the compound II. On the other hand, the formation of its derivatives indicate strongly the possible ionic character of chlorine in the molecule. The low solubility of compound in non-polar solvents supports this view. It could be therefore said that the P-Cl bond in compound II has a large percentage ionic character.

Three possible structures were proposed by Bezman and Smalley[48] for the compound II:





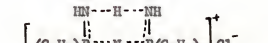


All of these, however, may be eliminated on the basis of the single peak in the nuclear magnetic resonance spectrum. It is believed that phosphonium chloride structures are more appropriate in view of the known

facts concerning this compound. Two such structures in which phosphorus atom are equivalent may be written for the compound II.

(a)

or its tautomer,



(b)

In structure (a) the pi bond is distributed over both bonds in the P-N-P group and in structure (b) all the P-N bonds have some multiple bond character, and one proton is held in a hydrogen bond between two nitrogen atoms. Both these structures are in accord with the fact that the chlorine is readily replaced by a variety of complex anions to give other salt-like derivatives. If, indeed, the 936 and 971 $cm.^{-1}$ bands in the infrared spectrum are attributable to a P-$\overset{H}{N}$-P group, structure (b) is to be preferred. However, this cannot be considered definite at the present.

Further support to the structure of compound II comes from the fact that this compound on pyrolysis gives diphenylphosphonitrilic polymers, predominantly the tetramer. This could happen by the intermolecular reaction of two molecules of compound II to give the tetramer:

It is rather difficult to state with certainty the mechanism for the reaction of diphenylchlorophosphine with ammonia and chloramine, but on the basis of two main products obtained in this reaction, the following steps seem to be reasonable.

$$(C_6H_5)_2PCl + 2NH_3 \longrightarrow (C_6H_5)_2PNH_2 + NH_4Cl \quad (1)$$

$$(C_6H_5)_2PNH_2 + NH_2Cl \longrightarrow \left[(C_6H_5)_2P(NH_2)_2\right]^+Cl^- \quad (2)$$

$$2\left[(C_6H_5)_2P(NH_2)_2\right]^+Cl^- \longrightarrow \left[(C_6H_5)_2\overset{NH_2}{\overset{|}{P}}{=}N{-}\overset{NH_2}{\overset{|}{P}}(C_6H_5)_2\right]^+Cl^- + NH_4Cl \quad (3)$$

Compound II

$$3\left[(C_6H_5)_2P(NH_2)_2\right]^+Cl^- \longrightarrow \left[(C_6H_5)_2PN\right]_3 + 3NH_4Cl \quad (4)$$

$$\left[(C_6H_5)_2PN\right]_3 + 3C_2H_2Cl_4 \longrightarrow \text{Compound I}$$

These reactions are in accordance with the proposed course of ammonolysis followed by chloramination of the diphenylchlorophosphine. The diphenylaminophosphine formed (equation 1) reacts with chloramine to form diphenyldiaminophosphonium chloride (equation 2). This intermediate was never isolated from the reaction, but its formation is an attractive assumption on the basis of the studies described in the Chapter I of this dissertation.

$$R_2R'P + NH_2Cl \longrightarrow \left[R_2R'PNH_2\right]^+Cl^-$$

It is assumed that the rate of the reaction of diphenylchlorophosphines with chloramine is slow as compared to the rate of its ammonolysis:

$$(C_6H_5)_2PCl + NH_2Cl \longrightarrow \left[(C_6H_5)_2\overset{NH_2}{\overset{|}{P}}{-}Cl\right]^+Cl^-$$

Under the high temperature conditions of this reaction and also because of the presence of two adjacent amino groups on the phosphorus atom, the proposed intermediate diphenyldiaminophosphonium chloride will not be a stable species. It is possible that three molecules of

diphenyldiaminophosphonium chloride lose three molecules of ammonium chloride to form the diphenylphosphonitrile trimer (equation 4), which crystallizes out as compound I because of the presence of tetrachloroethane (equation 5). The intermediate diphenyldiaminophosphonium chloride can also react intermolecularly, two molecules of the intermediate releasing one molecule of ammonium chloride to form the compound II (equation 3).

Because of the isolation of the only trimeric diphenylphosphonitrile (as compound I) rather than tetramer or higher species from the reaction, the following reaction seems to be quite important:

$$\left[(C_6H_5)_2\overset{NH_2}{\underset{|}{P}}{=}N{-}\overset{NH_2}{\underset{|}{P}}(C_6H_5)_2\right]^{+}Cl^{-} + \left[(C_6H_5)_2P(NH_2)_2\right]^{+}Cl^{-} \longrightarrow \left[(C_6H_5)_2PN\right]_3 + 2NH_4Cl \quad (6)$$

The isolation of two main products from the reaction compound I and compound II, rather than one or the other, may result from the three competing reactions as shown in equations 3, 4, and 6.

The above series of reactions help to explain the mechanism of diphenylchlorophosphine-ammonia and chloramine reaction. In addition to the above reactions (equation 1-6) there are some less important reactions which might be mentioned.

If it is assumed that the diphenylphosphonitrile monomer $\left[(C_6H_5)_2PN\right]$ has a transitory existence in the reaction, the following two reactions can also be considered:

$$\left[(C_6H_5)_2\overset{NH_2}{\underset{|}{P}}{=}N{-}\overset{NH_2}{\underset{|}{P}}(C_6H_5)_2\right]^{+}Cl^{-} + \left[(C_6H_5)_2PN\right] \longrightarrow \underset{NH_4Cl}{\left[(C_6H_5)_2PN\right]_3} + \quad (7)$$

$$\left[(C_6H_5)_2P(NH_2)_2\right]^{+}Cl^{-} + \left[(C_6H_5)_2PN\right] \longrightarrow \text{Compound II} \qquad (8)$$

A rather less important but a possible route for the formation of compound II in this reaction can be as follows:

$$2(C_6H_5)_2PNH_2 \longrightarrow (C_6H_5)_2P\text{-}\underset{\displaystyle H}{N}\text{-}P(C_6H_5)_2 + NH_3 \qquad (9)$$

$$(C_6H_5)_2P\text{-}\underset{\displaystyle H}{N}\text{-}P(C_6H_5)_2 + 2NH_2Cl \longrightarrow \left[(C_6H_5)_2\overset{\displaystyle NH_2}{P}\text{-}\underset{\displaystyle H}{\overset{\displaystyle NH_2}{N}}\text{-}P(C_6H_5)_2\right]^{++} 2Cl^{-}$$

$$\downarrow -HCl \qquad (10)$$

Compound II

At present there are no examples to support dichloramination but under the high temperature conditions of the reaction this certainly is a possibility. The diphosphonium compound (equation 10) can lose one molecule of hydrogen chloride under the existing basic conditions to form compound II (excess of ammonia is present in the reaction).

CHAPTER III

SYNTHESIS OF SOME N-SUBSTITUTED AMINODIBUTYLPHOSPHINES

Introduction

Purpose of Investigation

The N-substituted aminophosphines, $R_2N\text{-}PR_2$, are useful compounds as possible synthetic intermediates for the preparation of various organo-phosphorus compounds.

Recently, Sisler and Smith[60] prepared N-substituted aminodiphenylphosphines by the aminolysis of diphenylchlorophosphine. A corollary to this work, the present investigation was initiated to synthesize some N-substituted aminophosphines having alkyl groups substituted on the phosphorus atom. As an adjunct to this study, a new method for the preparation of dialkylchlorophosphines was investigated.

Historical Background

Michaelis in 1903,[14] prepared compounds of the type $R_2N\text{-}PCl_2$, by the partial aminolysis of phosphorus trichloride with various secondary amines or their hydrochlorides. Burg and Slota[61] prepared N-dimethylaminodimethylphosphine by the following reaction:

$$(CH_3)_2N\text{-}PCl_2 + 2(CH_3)_2MgBr \longrightarrow (CH_3)_2N\text{-}P(CH_3)_2 + 2MgBrCl$$

Issleib and Seidel[62] employed a similar procedure to prepare some N-diethyl aminophosphines having different groups substituted on the phosphorus atom.

Harris[63] and later, Sisler and Smith[60] prepared various N-substituted aminophosphines by the aminolysis of bis-(trifluoromethyl)-chlorophosphine and diphenylchlorophosphine, respectively.

A survey of the literature shows several methods for the preparation of dialkylchlorophosphines. A number of dialkylchlorophosphines were prepared by Plets[64] by the following reaction sequence:

$$R_3P{=}O + PCl_5 \longrightarrow \underset{\text{I}}{\left[R_3PCl_2\right]} + POCl_3$$

$$\underset{\text{I}}{\left[R_3PCl_2\right]} \longrightarrow R_2PCl + RCl$$

The intermediate (I) in the above reaction was not isolated but its presence was inferred from its decomposition to yield dialkylchlorophosphine.

Burg and Slota[61] prepared dimethylchlorophosphine by the treatment of HCl with N-dimethyleminodimethylphosphine. Later, Issleib and Seidel[62] extended this method for the preparation of diethyl-, dibutyl-, and dicyclohexyl-chlorophosphines.

The Russian chemists Komkov, Karavanov, and Ivin[65] prepared diethyl- and dibutyl-chlorophosphines by reducing the complex $(RR'PCl_2)^+(AlCl_4)^-$ with Al, K, or red phosphorus and KCl.

$$RCl + R'PCl_2 + AlCl_3 \longrightarrow \underset{\downarrow}{(RR'PCl_2)^+(AlCl_4)^-}$$
$$RR'PCl$$

$RPCl_2$ was prepared by reacting R_2Cd with PCl_3.

Maier[66] prepared dialkylbromophosphines in low yields (about 5 per cent) by allowing an alkyl halide to react with red phosphorus in presence of a copper catalyst:

$$RX + P_{red} \xrightarrow[\Delta]{Cu} R_2PCl + RPCl_2 + (PX)$$

Maier also prepared tetraalkyldiphosphines by the desulfuration of tetraalkyldiphosphinedisulfides using tri-n-butylphosphine.

$$R_2P(S)\text{-}P(S)R_2 + 2(C_4H_9)_3P \longrightarrow R_2P\text{-}PR_2 + 2(C_4H_9)_3PS$$

The P-P bond in the tetraalkyldiphosphines was cleaved by treating it with theoretical amount of chlorine or bromine in benzene solution to yield the dialkylhalophosphines.

$$R_2P\text{-}PR_2 + Cl_2 \longrightarrow 2R_2PCl$$

Recently, Parshall[67] prepared dimethylchlorophosphine by the simultaneous cleavage and reduction of tetramethyldiphosphinedisulfide with phenyldichlorophosphine.

$$(CH_3)_2P(S)\text{-}P(S)(CH_3)_2 + PCl_2 \longrightarrow 2(CH_3)_2PCl + (\phi PS)$$

The nature of the by-product (ϕPS) in this reaction was not discussed.

Maier[66] prepared dimethylchlorophosphine by the desulfuration of dimethylthionophosphinic chloride using tri-n-butylphosphine.

Materials

Di-n-butylchlorophosphine was initially prepared by the procedure of Plets.[64] Later on, it was prepared by the desulfuration of di-n-butylthionophosphinic chloride using tri-n-butylphosphine. The

tri-n-butylphosphine was obtained from Food and Machinery Chemicals and found to be of sufficient purity for the present investigation. Di-n-propylamine was obtained from Union Carbide Chemicals. t-Butylamine obtained from Rohm and Haas was used after redistillation. Piperidine was obtained from Eastman Organic Chemicals and used after redistillation. Reagent grade aniline was obtained from Fisher Scientific Company. Anhydrous ether kept over sodium was used throughout this investigation. The nitrogen gas used for the dry box was Airco prepurified grade.

All boiling points and melting points were uncorrected. Unless otherwise stated, the elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee.

Experimental and Results

Preparation of Dialkylchlorophosphines

Preparation of Di-n-butylchlorophosphine by Plets Method. The tri-n-butylphosphine oxide used in this preparation was prepared by the oxidation of tri-n-butylphosphine with 40 per cent warm nitric acid[68] and purified by distillation under reduced pressure. In an representative experiment, 52.0 grams of tri-n-butylphosphine oxide (0.24 mole) was placed in a 250 ml. round-bottom reaction flask equipped with a thermometer well. To this, 51.0 grams of phosphorus pentachloride (0.24 mole) was added in small increments under nitrogen at room temperature. During the addition of phosphorus pentachloride the temperature of the mixture in the reaction flask rose up to 120°C. After all the phosphorus pentachloride was added, the mixture was allowed to cool to room temperature. The reaction flask was then fitted with a fractionating column and a distillation head. The system was flushed with dry

nitrogen, and oxygen, and moisture was prevented from entering the system by means of a nitrogen lock. The mixture was then gradually heated. As the temperature of the mixture gradually increased, the low boiling by-products of the reaction distilled off. The temperature of the mixture slowly reached as high as 230°C., during which time 20.6 grams of low boiling distillate was collected at various distilling temperatures. These by-products were discarded without any identification. The remaining products in the reaction flask were distilled under reduced pressure, using a nitrogen bleeder. A total of 12.3 grams of colorless liquid was distilled at 121-123°C./4 mm. A second portion of 3.5 grams was collected at 125-128°C./4 mm. The chloride contents of the first fraction was determined after hydrolyzing a sample with dilute HNO_3. It contained 19.35 per cent chlorine. Calculated for $(C_4H_9)_2PCl$: 19.7 per cent. This indicated that the liquid obtained was essentially di-n-butylchlorophosphine. (Yield: 37 per cent). The reported boiling points were 120-125°C./15 mm.[64] and 216-217°C./760 mm.[62]

The infrared spectrum of the above prepared di-n-butylchlorophosphine showed a strong absorption band in the region 1190 to 1250 $cm.^{-1}$. This absorption was in the reported region for the P→O bond,[69] thus indicating that the product obtained in the above reaction contained an oxide impurity. This impurity could either result from the partial conversion of di-n-butylchlorophosphine to its oxide $(C_4H_9)_2P(O)Cl$, or it could result from the presence of tri-n-butylphosphine oxide in the distillate.

Preparation of Diethylchlorophosphine and Di-n-butylchlorophosphine by the Combined Parshall-Maier Method. By heating a mixture

of tetramethyldiphosphinedisulfide and phenyldichlorophosphine (mole ratio 1:3) at about 200°C. dimethylchlorophosphine was prepared by Parshall.[67] We made attempts to prepare diethylchlorophosphine and di-n-butylchlorophosphine using Parshall's procedure. On heating a mixture of tetraethyldiphosphinedisulfide and phenyldichlorophosphine in the mole ratio 1:3 up to 220-230°C., diethylchlorophosphine was not obtained. Similarly, di-n-butylchlorophosphine was not obtained on heating a mixture of tetra-n-butyldiphosphinedisulfide and phenyldichlorophosphine in the mole ratio of 1:3 up to 240-245°C. In these reactions, however, the thermal conditions employed cleaved the P-P bond in the diphosphinedisulfides to yield the corresponding dialkylthionophosphinic chlorides $R_2P(S)Cl$, almost quantitatively.

$$4R_2P(S)\text{-}P(S)R_2 + 4\phi PCl_2 \longrightarrow 8R_2P(S)Cl + (\phi P)_4$$

In the above mentioned reactions the cleavage of P-P occurred even at lower temperatures. In the case of tetraethyldiphosphinedisulfide the cleavage of P-P occurred around 160°C. In the case of tetra-n-butyldiphosphinedisulfide, similar results were obtained at 205-210°C.

It was also found that the dialkylthionophosphinic chloride could be prepared by using 1:1 mole ratio of tetraalkyldiphosphinedisulfides and phenyldichlorophosphine. This mole ratio was preferred especially in the case of tetraethyldiphosphinedisulfide reaction. This was due to the difficulty in separation of diethylthionophosphinic and phenyldichlorophosphine, which had close boiling points.

From the yellow residue in the above reaction, tetraphenylcyclo-tetraphosphine $(\phi P)_4$, was isolated and identified.

By using Maier's method,[66] desulfuration of dialkylthionophosphinic chlorides $R_2P(S)Cl$, was carried out using tri-n-butylphosphines.

$$R_2P(S)Cl + (C_4H_9)_3P \longrightarrow R_2PCl + (C_4H_9)_3P(S)$$

Below are described two representative experiments for the preparation of diethylchlorophosphine and di-n-butylchlorophosphine. The tetraethyl- and tetra-n-butyl-diphosphine-disulfides were prepared by the reaction of $P(S)Cl_3$ and appropriate Grignard reagents.[70]

Diethylchlorophosphine. The reaction of tetraethyldiphosphinedisulfide and phenylchlorophosphine was carried out in a 100 ml. round-bottom reaction flask equipped with a thermometer well. The reaction flask was fitted with a fractionating column and a distillation head. The entire apparatus was flushed with dry nitrogen prior to use and during the reaction oxygen and moisture were prevented from entering the system by means of a nitrogen lock. Four and five tenths grams of tetraethyldiphosphinedisulfide (0.0186 mole) and 3.4 grams of phenyldichlorophosphine (0.0191 mole) were mixed in the reaction flask. The reaction flask was then gradually heated. At about 130°C. the mixture became homogeneous and assumed a yellowish color. The mixture was heated up to approximately 160°C. The resultant products were cooled and distilled under reduced pressure. Five grams of colorless, clear liquid was collected at 49-50°C./0.3 mm. This was identified as diethylthionophosphinic chloride, $(C_2H_5)_2P(S)Cl$. (Yield: 86 per cent) The refractive index at 25°C. was 1.5295. The reported values of the boiling point of $(C_2H_5)_2P(S)Cl$ were 117-120°C./15 mm.,[64] 92-93°C./6 mm. and the refractive index at 20°C. was 1.5286.[65]

A dark yellow residue remained in the reaction flask along with some undistilled liquid. The residue was treated with methanol and quickly filtered to separate the liquid portion. The yellow colored solid thus obtained was vacuum dried. It melted at 140-141°C. The infrared absorption spectrum of this yellow solid was identical with one obtained for the tetraphenylcyclotetraphosphine by Kuchen and Buchwald.[71] They have reported the melting point of an analytical pure sample as 150.5°C. The yellow solid was analyzed for phosphorus without any attempts to purify it.

Calcd. for $(\phi P)_4$: P, 28.66

Found: P, 25.65

The desulfuration of the diethylthionophosphinic chloride was accomplished by using tri-n-butylphosphine. The apparatus used for this reaction was essentially the same as described earlier in this experiment. Five grams of diethylthionophosphinic chloride (0.0319 mole) and 10.0 grams of tri-n-butylphosphine (0.033 mole, about 10 per cent excess over 1:1 mole ratio) were mixed in the 100 ml. reaction flask. The mixture was slowly heated under a nitrogen lock. The reaction seemed to take place at about 180°C. as noticed by the appearance of yellow color and a whirling motion in the mixture. The homogeneous yellow colored mixture on distillation gave 1.2 grams of colorless liquid at and around 134°C. The liquid strongly fumed in air. This liquid was identified as diethylchlorophosphine. The refractive index at 20°C. was 1.4722. The reported refractive index at 20°C. was 1.472.[65] The reported boiling points were 60-70°C./15 mm.,[64] 61-62°C./72 mm.,[65] and 133-134°C./760 mm.[62] The yield of the diethylchlorophosphine was 30 per cent.

Di-n-butylchlorophosphine. The reaction of tetra-n-butyldiphosphinedisulfide and phenyldichlorophosphine was carried out in a 250 ml. round-bottom reaction flask equipped with a thermometer well. The reaction flask was fitted with a fractionating column and a distillation head. The entire apparatus was flushed with dry nitrogen gas prior to use, and during the reaction, oxygen and moisture were prevented from entering the system by means of a nitrogen lock. Twenty-four grams of tetra-n-butyldiphosphinedisulfide (0.068 mole) and 37.0 grams of phenyldichlorophosphine (0.206 mole) were mixed in the reaction flask. The mixture was gradually heated to a maximum temperature of 210°C. and maintained at this temperature for about two hours. A yellow homogeneous mixture was obtained. The products on distillation at reduced pressure gave 26.5 grams of colorless clear liquid boiling at 74-76°C./0.2 mm. The refractive index at 25°C. was 1.5128. This liquid was identified as di-n-butylthionophosphinic chloride, (yield: 91 per cent). It gave the following elemental analysis:

Calcd. for $(C_4H_9)_2PSCl$: C, 45.17; H, 8.53; P, 14.56; S, 15.07; Cl, 16.67

Found: C, 45.48; H, 8.60; P, 14.29; S, 14.78; Cl, 16.91

The reported boiling point of $(C_4H_9)_2P(S)Cl$ was 155-159°C./15 mm.[64]

Desulfuration of the di-n-butylthionophosphinic chloride was done using tri-n-butylphosphine. The apparatus set up for this experiment was identical with one described earlier. Sixteen grams of di-n-butylthionophosphinic chloride (0.075 mole) and 16.8 grams of tri-n-butylphosphine (0.083 mole, about 10 per cent excess over 1:1 mole ratio) were mixed in the reaction flask. The mixture was gradually heated to 180°C. under a nitrogen lock. This temperature was maintained for two hours. On distilling the reaction products at reduced pressure,

11.1 grams of di-n-butylchlorophosphine was obtained at 49-50°C./0.2 mm. (yield 82 per cent). The refractive index at 25°C. was 1.4805. The reported boiling points for the di-n-butylchlorophosphines were 120-125°C./15 mm.,[64] 91-92°C./12 mm., and 216-217°C./760 mm.[62]

Preparation of N-Substituted Aminodi-(-n-butyl)-phosphine

Outline of Procedure. Since di-n-butylchlorophosphine and the prepared aminophosphines are reactive towards oxygen and moisture, it was necessary to take special precautions to insure anhydrous and oxygen-free conditions. All reactions were carried out in the dry box in a nitrogen atmosphere. The box was a two-compartment lucite box with neoprene gloves. The prepurified nitrogen gas used in the dry box was passed through sulfuric acid and packed columns of magnesium perchlorate and Drierite. Traces of oxygen were removed by passing the nitrogen gas through a 10" x 1" packed column of metallic copper heated to 400°C. In addition to this, a few open dishes containing phosphorus (V) oxide were placed in the dry box. The anhydrous ether, previously kept over sodium, was used in all the reactions.

The ether solution of the amine was placed in a two-necked round-bottom reaction flask fitted with a dropping funnel. The chlorophosphine, also in ether solution, was added to the amine dropwise. The reaction mixture was stirred by means of a magnetic bar placed inside the reaction flask. All the reactions were carried out at room temperature. After all the chlorophosphine was added, the mixture was stirred for some additional time to insure the completion of the reaction. The reaction products were filtered inside the dry box, and the solids were washed with additional amounts of ether. The volume of the combined filtrate and washings was reduced inside the dry box under diminished

pressure. The ether solution was transferred to a 50 ml. distillation flask. This ether solution was then distilled in a semi-micro distillation assembly outside the dry box. The aminophosphine collected was always stored under dry nitrogen.

The analytical samples of the aminophosphines were filled in the dry box. Separate samples were made for the analysis of each element. The cells for running the infrared spectra were also filled in the dry box. The methyl iodide derivatives of the aminophosphines were prepared in ether solution inside the dry box.

All saturated hydrocarbon groups referred to hereafter are normal unless stated otherwise.

N-dipropylaminodibutylphosphine. A solution of 4.1 grams of dibutylchlorophosphine (22.7 mmoles) in 50 ml. of ether, was added with constant stirring, to 4.7 grams of dipropylamine (46.5 mmoles) in 75 ml. of ether. After the completion of the reaction, 2.8 grams of the amine-hydrochloride was obtained (calculated for $(C_3H_7)_2NH_2$ Cl: 3.1 grams). The ether solution on distillation gave 3.2 grams of colorless liquid boiling at 84°C./0.5 mm. The refractive index at 25°C. was 1.4620. Analytical data confirmed the formula: $(C_3H_7)_2N\text{-}P(C_4H_9)_2$. (Yield: 57 per cent.)

Calcd. for $(C_3H_7)_2N\text{-}P(C_4H_9)_2$: C, 68.44; H, 13.13; P, 5.70; N, 12.61

Found: C, 68.36; H, 13.28; P, 5.96; N, 12.75

The infrared absorption spectrum of this compound showed no oxide impurity. The identity of the product was further established by the analysis of the methyl iodide adduct of the aminophosphine.

Methyl Iodide Adduct of N-Dipropylaminodibutylphosphine. The methyl iodide adduct of N-dipropylaminodibutylphosphine was prepared by

mixing the ethereal solutions of the aminophosphine and methyl iodide at room temperature. A white precipitate separated out immediately. It was filtered, washed with additional amounts of ether, and vacuum dried. The white shining solid melted at 116-117°C. The iodide analysis of this solid showed it to be a 1:1 adduct of the aminophosphine and methyl iodide.

Calcd. for $(C_3H_7)_2N\text{-}P(C_4H_9)_2 \cdot CH_3I$: I, 32.74

Found: I, 33.39

t-Butylaminodibutylphosphine. A solution of 3.5 grams of dibutylchlorophosphine (19.4 mmoles) in 50 ml. of ether was added dropwise, over a period of one hour, to 2.9 grams of t-butylamine (39.7 mmoles) in 100 ml. of ether. The mixture was constantly stirred during the course of the reaction. After the completion of the reaction the solids were filtered and washed with ether. The total solids weighed 2.0 grams (calculated for $t\text{-}C_4H_9NH_2$ Cl: 2.1 grams). The filtrate and the washings were distilled to give 2.1 grams of a colorless liquid boiling at 67°C./0.35 mm. The refractive index at 25°C. was 1.4562. The analytical data confirms the formula $(t\text{-}C_4H_9)NHP(n\text{-}C_4H_9)_2$ (yield: 51 per cent).

Calcd. for $(t\text{-}C_4H_9)NHP(n\text{-}C_4H_9)_2$: C, 66.31; H, 12.99; P, 14.25; N, 6.45

Found: C, 66.31; H, 12.74; P, 14.38; N, 6.80

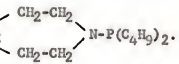
The infrared absorption spectrum showed a weak absorption peak at 3350 $cm.^{-1}$ for N-H stretching vibration. The spectrum indicated no oxide impurity in the sample. The identity of the aminophosphine was further established by the analysis of its methyl iodide adduct.

Methyl Iodide Adduct of t-Butylaminodibutylphosphine. The methyl iodide adduct of t-butylaminodibutylphosphine was prepared by mixing the ethereal solutions of the aminophosphine and methyl iodide at room temperature. A white turbidity appeared immediately upon mixing, and, upon standing, a white solid separated out from the solution. It was filtered, washed with ether and vacuum dried. The white solid melted at 116-118°C. The iodine analysis of this compound confirmed the formation of a 1:1 adduct of the aminophosphine and methyl iodide.

Calcd. for $t\text{-}C_4H_9)NHP(n\text{-}C_4H_9)_2 \cdot CH_3I$: I, 35.26

Found: I, 34.71

Piperidinodibutylphosphine. A solution of 6.2 grams of dibutylchlorophosphine (34.3 mmoles) in 75 ml. of ether was added dropwise to 5.8 grams of piperidine (78.2 mmoles) in 100 ml. of ether, over a period of two hours. After the completion of the reaction, the aminehydrochloride was filtered, and it weighed 4.2 grams (calculated for $C_5H_{10}NH_2$ Cl: 4.2 grams). The ether solution on distillation gave 3.9 grams of colorless liquid boiling at 82°C./0.1 mm. The refractive index at 20°C. was 1.4775. The analytical data confirm the formula:



Calcd. for $C_5H_{10}N\text{-}P(C_4H_9)_2$: P, 13.67; N, 5.97

Found: P, 13.51; N, 6.12

The infrared spectrum of this aminophosphine showed no oxide impurity in the compound. The identity of the aminophosphine was further confirmed by the analysis of its methyl iodide adduct.

Methyl Iodide Adduct of Piperidinodibutylphosphine. The methyl iodide adduct of piperidinodibutylphosphine was prepared by mixing the ethereal solutions of the aminophosphine and methyl iodide at room temperature. The white solid thus obtained was filtered, washed with ether, and vacuum dried. It melted at 162-164°C. The iodine analysis of this compound proves it to be a 1:1 adduct of the aminophosphine and the methyl iodide.

Calcd. for
$C_5H_{10}N\text{-}P(C_4H_9)_2 \cdot CH_3I$: I, 34.18

Found: I, 34.04

Anilinodibutylphosphine. A solution of 6.0 grams of dibutylchlorophosphine (32.6 mmoles) in 75 ml. of ether was added dropwise to 6.2 grams of aniline (66.7 mmoles) in 100 ml. of ether. After the completion of the reaction, the reaction products were filtered. The aminehydrochloride isolated weighed 4.1 grams, and it melted at 195-196°C. (calculated for $(C_6H_5)NH_3$ Cl: 4.3 grams). The literature value of the melting point was 198°C. The ether solution was distilled under reduced pressure. One and seven tenths grams of liquid was collected at various distilling temperatures as the fore-run, and it was not identified. A colorless viscous liquid was collected at 140-144°C./0.3 mm. (4.0 grams). The refractive index at 20°C. was 1.5304.

The elementary analysis of this liquid was:

Calcd. for
$C_6H_5NHP(C_4H_9)_2$: C, 70.85; H, 10.19; P, 13.05; N, 5.91

Found: C, 66.42; H, 10.49; P, 15.72; N, 5.55

The infrared absorption spectrum of this product showed weak absorption peaks at 3390 and 3270 $cm.^{-1}$ corresponding to mono-substituted phenyl and N-H stretching vibration. It did not show any impurity of oxide in the product.

The carbon and phosphorus contents of this product did not agree with the theory. Therefore a second experiment was carried out under similar conditions to prepare anilinodibutylphosphine. In this case the liquid distilling at 136-140°C./0.25 mm. was analyzed. The refractive index at 20°C. was 1.5264.

Calcd. for $(C_6H_5)NHP(C_4H_9)_2$: C, 70.85; N, 10.19; P, 13.05; N, 5.91

Calcd. for $(C_6H_5)N\left[P(C_4H_9)_2\right]_2$: C, 69.26; H, 10.83; P, 16.24; N, 3.67

Found: C, 66.45; H, 10.68; P, 15.99; N, 4.02

The infrared absorption spectrum of the product obtained from the second experiment was identical with one obtained in the first experiment. No solid methyl iodide adduct of the product was obtained. A white turbidity was obtained on mixing the ethereal solution of methyl iodide and the above product. On standing, a white viscous liquid, also turbid in appearance, separated out from the ether solution.

From the above results, it seems quite probable that a mixture of anilinodibutylphosphine and N,N-bis-(dibutylphosphino)-aniline, $(C_6H_5)N\left[P(C_4H_9)_2\right]_2$ was obtained in the above two reactions.

Discussion

N-Substituted aminodi-n-butylphosphines were prepared by the aminolysis of di-n-butylchlorophosphine. These results show that the aminolysis reactions of dialkylchlorophosphines may be employed for the preparation of various substituted aminophosphines.

The structural confirmation of the aminophosphines was obtained by their elementary analyses, infrared spectra, and the formation of their 1:1 adducts with methyl iodide. No definite assignment for the P-N bond

absorption could be made from the infrared spectra of these compounds. This results from the presence of broad absorption bands in the 680-800 cm.$^{-1}$ region of these spectra. The absorption for the P-N bond is reported at 680-750 cm.$^{-1}$.[72] The infrared spectra, on the other hand, clearly indicate any impurity of aminophosphine oxide present in the parent aminophosphine by the appearance of a strong absorption band at about 1190 cm.$^{-1}$. To some extent this band was useful in estimating the purity of the prepared sample.

The aminophosphines are very susceptible to reaction with oxygen or moisture. They are easily converted to their corresponding oxides. The formation of the aminophosphine oxide can be followed by the study of infrared spectra. In general it was noticed that the aminophosphine oxides are appreciably soluble in their parent aminophosphines. This solubility effect made their separation somewhat difficult.

The aminophosphines formed 1:1 adducts with methyl iodide at room temperature. It seems that the low solubility of these adducts in ether solution prevented their further reaction with the methyl iodide. It is quite possible that under higher temperature conditions and in a proper solvent, these aminophosphines would form 1:2 adducts with methyl iodide. It has been shown by Burg and Slota[61] that the CH_3 group is attached to the phosphorus atom in the 1:1 adduct of N-dimethylaminodiemthyl-phosphine and methyliodide. No stidues were made to locate the position of the methyl group in our aminophosphine-methyl iodide adducts. It seems quite reasonable to assume that the methyl group in these adducts is attached to the phosphorus atom because of its increased base strength as compared with nitrogen. In the aminophosphines, both nitrogen

and phosphorus atoms contain a lone electron pair. Because of the availability of d orbitals in case of phosphorus, there would be a considerable π electron donation from the nitrogen to the d orbitals of phosphorus. This would increase the base strength of the phosphorus atom in the molecule as compared with nitrogen.

This study also resulted in the finding of a new method for the preparation of dialkylchlorophosphines. This method involves the cleavage of tetraalkyldiphosphinedisulfides with phenyldichlorophosphine to form the dialkylthionophosphinic chlorides, which can be desulfurated by tri-n-butylphosphine to give the dialkylchlorophosphines.

Tetraphenyl-cyclo-tetraphosphine was isolated from the reaction of tetraalkyldiphosphinedisulfides with phenyldichlorophosphine.

$$4R_2(S)P\text{-}P(S)R_2 + 4\phi PCl_2 \longrightarrow 8R_2PCl + (\phi P)_4$$

The simultaneous cleavage and desulfuration of tetramethyl-diphosphinedisulfide using phenyldichlorophosphine was carried out by Parshall:

$$(CH_3)_2P(S)\text{-}P(S)(CH_3)_2 + \phi PCl_2 \longrightarrow (CH_3)_2PCl + (\phi PS)$$

The nature of the by-product (ϕPS) in the above reaction was not mentioned. From the results obtained in this investigation, it seems quite reasonable that the first step in the Parshall's reaction was the cleavage of P-P bond:

$$4(CH_3)_2P(S)\text{-}P(S)(CH_3)_2 + 4\phi PCl_2 \longrightarrow 8(CH_3)_2P(S)Cl + (\phi P)_4$$

The mechanism of the second step in Parshall's reaction which was the removal of sulfur from $(CH_3)_2P(S)Cl$ is not clear. The

$(CH_3)_2P(S)Cl$ was desulfurated either by its reaction with phenyldichlorophosphine (which was present in excess) or by $(\phi P)_4$ which was formed as in the first step mentioned above.

It was shown by the present investigation that the desulfuration of dialkylthionophosphinic chlorides (other than methyl) could not be achieved either by phenyldichlorophosphine or $(\phi P)_4$ which was formed in these reactions. Even at higher temperatures than employed by Parshall, both of these compounds failed to remove sulfur from diethyl- and dibutylthionophosphinic chlorides. This may be related to the possible higher P→S bond strength in the diethyl- and dibutylthionophosphinic chlorides as compared with dimethylthionophosphinic chlorides. The desulfuration was carried out using tri-n-butylphosphine.

BIBLIOGRAPHY

1. Raschig, F., Ber, 40, 4580 (1907).
2. Raschig, F., Z. anorg. Chem., 20, 2068 (1907).
3. Audrieth, L. F., and Diamond, L. H., J. Am. Chem. Soc., 76, 4869 (1954).
4. Audrieth, L. F., and Diamond, L. H., J. Am. Chem. Soc., 77, 3131 (1955).
5. Sisler, H. H., and Mattair, R., J. Am. Chem. Soc., 73, 1619 (1951).
6. Sisler, H. H., et al., J. Am. Chem. Soc., 78, 3874 (1956).
7. Sisler, H. H., and Omietanski, G., J. Am. Chem. Soc., 78, 1211 (1956).
8. Sarkis, A., Dissertation Abstr., 17, 1458 (1957).
9. Sisler, H. H.,and Omietanski, G., Inorg. Syntheses, V, 91 (1957).
10. Staudinger, H., and Hauser, E., Helv. Chim. Acta., 4, 861 (1921).
11. Staudinger, H., and Mayer, J., Helv. Chim. Acta., 2, 635 (1919).
12. Mann, F. G., and Chaplin, E.J., J. Chem. Soc., 1937, 527.
13. Kirsanov, A. V., and Nekrasov, Z. D., Zhur. Obschei. Khim., 26, 903 (1956). (C. A., 50, 1463 (1956).)
14. Michaelis, A., Ann., 326, 129 (1903); ibid., 315, 43 (1901).
15. Goldschmidt, S., and Krauss, H. L., Ann., 595, 193 (1955).
16. Horner, L., and Oediger, H., Ann., 627, 142 (1959).
17. Appel, R., Buchner, W., and Guth, E., Ann., 618, 53 (1958).
18. Appel, R., and Hauss, A., Chem. Ber., 93, 405 (1960).
19. Sisler, H. H., et al., J. Am. Chem. Soc., 81, 2982 (1959); Sisler, H. H., Ahuja, H. S., and Smith, N. L., J. Org. Chem., 26, 1819 (1961).

20. Gruttner, G., and Wiernik, M., Ber, 48, 1473 (1915); Gruttner, G., and Krause, E., Ber, 49, 437 (1916).

21. Hinton, R., and Mann, F. G., J. Chem. Soc., 1959, 2835.

22. Jones, W., et al., J. Chem. Soc., 1947, 1448.

23. Audrieth, L. F., Colton, E., and Jones, J., J. Am. Chem. Soc., 76, 1428 (1954).

24. Jander, J., Z. anorg. u. allgem. Chem., 280, 264 (1955); ibid., 280, 276 (1954).

25. Cahn, J. W., and Powell, R. E., J. Am. Chem. Soc., 76, 2565 (1954).

26. Drago, R. S., and Sisler, H. H., J. Am. Chem. Soc., 77, 3191 (1955).

27. Stokes, H. M., Am. Chem. J., 17, 275 (1895); ibid., 19, 782 (1897).

28. Liebig, J., Ann., 11, 139 (1834).

29. Gerhardt, C., Ann. Chem. Phys., 3 18, 188 (1846); Compt. rend., 22, 858 (1846).

30. Laurent, A., Compt. rend., 31, 356 (1850).

31. Gladstone, J. H., and Holmes, J. D., J. Chem. Soc., 17, 225 (1864).

32. Audrieth, L. F., Steinman, R., and Toy, A. D. F., Chem. Revs., 32, 109 (1943).

33. Schenk, R., and Romer, G., Ber, 57B, 1343 (1924).

34. Steinman, R., Schirmer, F. B., and Audrieth, L. F., J. Am. Chem. Soc., 64, 2377 (1942).

35. Bode, H., Z. anorg. Chem., 252, 133 (1943).

36. Bean, and Shaw, R. A., Chem. and Ind., 1189 (1960).

37. Seel, F., and Langer, J., Angew. Chem., 68, 461 (1956).

38. Ratz, R., and Grundmann, C., J. Inorg. and Nuclear Chem., 16, 60 (1960).

39. Schmitz-Dumont, O., and Kulkens, H., Z. anorg. Chem., 238, 189 (1938).

40. Chapman, A. C., et al., J. Chem. Soc., 1960, 3608.

41. Paddock, N. L., and Searle, H. T., Advances in Inorganic Chemistry and Radiochemistry, Vol. I, Academica Press, New York, 1959.

42. Searle, H. T., Proc. Chem. Soc., 1959, 7.

43. Rosset, H., Compt. rend., 180, 750 (1952).

44. Bode, H., and Bach, H., Ber, 75B, 215 (1942).

45. Shaw, R. A., and Stratton, C., Chem. and Ind., 1959, 52.

46. Bode, H., and Themer, R., Ber, 76B, 121 (1943).

47. Haber, C. P., Herring, D. L., and Lawton, E. A., J. Am. Chem. Soc., 80, 2116 (1958).

48. Bezman, I. I., and Smalley, J. H., Chem. and Ind., 1960, 839.

49. Brockway, L. O., Bright, W. M., J. Am. Chem. Soc., 65, 1551 (1943).

50. Ketelaar, J. A. A., and de Vries, T. A., Rec. trav. chim., 58, 1081 (1939).

51. Craig, D. P., Chem. and Ind., 1958, 3.

52. Craig, D. P., and Paddock, N. L., Nature, 1959, 1081.

53. Gilman, H., and Brown, G. E., J. Am. Chem. Soc., 67, 825 (1945).

54. Kuchen, W., and Buchwald, H., Angew. Chem., 68, 307 (1957).

55. Daasch, L. W., J. Am. Chem. Soc., 76, 3403, (1954).

56. Von Becher, H. J., and Seel, F., Z. anorg. u. allgem. Chem., 305, 148 (1960).

57. Shaw, R. A., Chem. and Ind., 1959, 54.

58. Von Buhler, K., and Bues, W., Z. anorg. u. allgem. Chem., 308, 62 (1961).

59. Daasch, L. W., and Smith, D.C., Anal. Chem., 23, 853 (1951).

60. Sisler, H. H., and Smith, N. L., J. Org. Chem., 26, 611 (1961).

61. Burg, A. B., and Slota, P. J., J. Am. Chem. Soc., 80, 1107 (1958).

62. Issleib, K., and Seidel, W., Chem. Ber., 92, 2681 (1959).

63. Harris, G., J. Chem. Soc., 1959, 512.

64. Plets, V. M., Dissertation Kazan, 1938. Cited by Kosolapoff, G. M., Org. Reactions, Vol. VI, p. 319, John Wiley & Sons, New York, 1951.

65. Komkov, I. P., Karavanov, K. V., and Ivin, S. Z., J. Gen. Chem., USSR, 28, 2992 (1958).

66. Maier, L., Angew. Chem., 71, 574 (1959); Maier, L., Personal communications.

67. Parshall, G. W., J. Inorg. and Nucl. Chem., 12, 372 (1960).

68. Davis, W. C., and Jones, W. J., J. Chem. Soc., 1929, 33.

69. Berlin, K. D., and Butler, G., Chem. Revs., 60, 261 (1960).

70. Issleib, K., and Tzschach, A., Chem. Ber., 92, 704 (1959).

71. Kuchen, W., and Buchwald, H., Chem. Ber., 91, 2296 (1958).

72. Holmstedt, B., and Larsson, L., Acta. Chem. scand., 5, 1179 (1951).

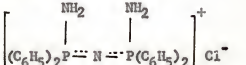
APPENDIX

Proton Magnetic Resonance Studies of Compound II

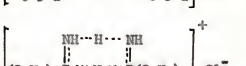
$[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$

(Chapter II)

Proton magnetic resonance spectrum of compound II was run in deuterated chloroform solution in a Varian high resolution spectrometer, operating at a frequency of 60 megacycles. Benzene was used as an internal reference. A complex pattern in the benzene region, having a relative area of 4.8 was assigned to phenyl groups. A single broad peak corresponding to a chemical shift of 1.3 p.p.m. to high field from the benzene reference, and having a relative area of 1.0 was assigned to the protons on the nitrogen atoms. The presence of a single peak and with a relative area equivalent to four protons, indicate that these protons have identical environment. On this basis the structure (a) for the compound II, where the pi bond is distributed over the P-N-P group is preferred to structure (b).



(a)



(b)

BIOGRAPHICAL SKETCH

Harbhajan Singh Ahuja was born in Peshawar (Pakistan) on July 11, 1930. He attended N. S. S. Khalsa High School at Peshawar. Unfortunately, because of the political disturbances in the pre-partition days of India, he could not complete his final high school examination held in March, 1947. In April, 1947, his family moved to Bombay (India) from where he appeared and passed Matriculation examination held by East Punjab University in February, 1948. He joined Elphistone College, Bombay, in 1949, and later transferred to the Institute of Science, Bombay, for his final degree examination. Both these institutions are affiliated to the University of Bombay. He received his Bachelor's degree with honors in Chemistry in August, 1953, from the University of Bombay. He joined Khalsa College, also affiliated to the University of Bombay, for his graduate work. He received his Master's degree in Inorganic Chemistry (by papers) in August, 1956, from the University of Bombay. He joined the University of Florida in the fall of 1957.

During the period 1954-1957, he served in Khalsa College first as a part-time and later as a full-time instructor in Chemistry. At the University of Florida he served as a research assistant on a project sponsored by W. R. Grace and Company through a contract with the University of Florida

The author is a member of the American Chemical Society and Alpha Chi Sigma fraternity.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

February, 1962

Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:

Chairman